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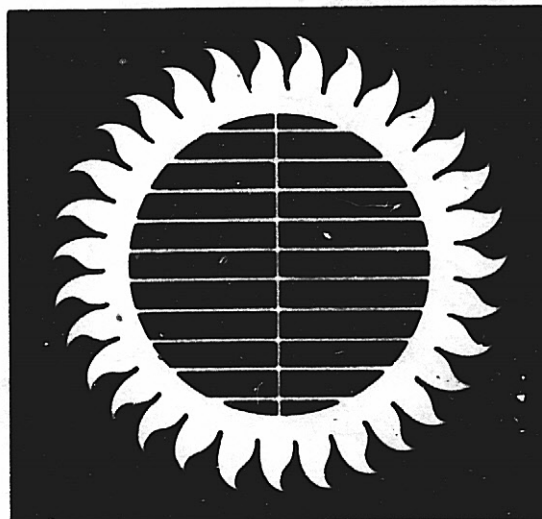
# Workshop Proceedings

# Photovoltaic Conversion of Solar Energy for Terrestrial Applications

Vol. II. Invited Papers

October 23-25, 1973  
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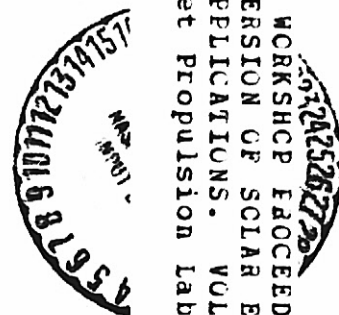
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**SESSION I**  
**SINGLE-CRYSTAL SILICON**

## **SESSION I. SINGLE-CRYSTAL SILICON**

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**SILICON CELLS—J. Lindmeyer**

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**A PROPOSED SCHEME FOR THE VLS GROWTH OF SINGLE-CRYSTAL SILICON SHEETS—  
A. S. Blum**

## SILICON PHOTOVOLTAIC DEVICE DEVELOPMENT PLAN

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### Presentation Summary

The potential for using silicon solar cells to provide large amounts of electrical power has been well established (Ref. 1). Also a proposed plan has been prepared which showed other potential applications and methods for achieving system cost reductions (Refs. 2 and 3). Figure 1 shows a schematic drawing of some typical applications for photovoltaic power systems and indicates how the size of these systems might increase as a function of time.

To make it possible to achieve large scale utilization of photovoltaic systems, a well balanced R&D plan must be supported. Such a proposed program was prepared and is summarized in Fig. 2 (Ref. 4). The plan shows various specific photovoltaic concepts that have validity for study, with large scale demonstrations being projected for the 1985-1990 time period. Each of these concepts has its own particular set of development steps, budgets, and milestones which must be analyzed and evaluated separately. There are, however, a set of basic photovoltaic development tasks that are common to all and can be carried out parallel to the concept development. These tasks can be planned and carried out independently with new technology being fed into the various conceptual systems as they become available. The basic studies are summarized into the five task categories shown, although the reference gives detailed tasks within each category. Some of the anticipated technology outputs are shown in the chart, although there will obviously be more. It is estimated that these tasks would require a budget of \$12 to 20 million per year for the next 10 years.

The key factors involved in reducing photovoltaic power system costs are shown in Fig. 3. The price of pure silicon is critical if polycrystalline material is to be used, but not so critical if the gaseous compound (trichlorosilane or silane) is used directly. New single-crystal silicon growing techniques, such as ribbons or sheets, would by-pass the expensive ingot growing, cutting, slicing, and polishing process now used. A great deal can be done with the device fabrication process to decrease costs. This will be discussed in more detail below. Array fabrication and packaging must be done with inexpensive materials and processes that utilize the tremendous knowledge and machinery presently available in the packaging industry. Concentration of sunlight on a photovoltaic device can be an important tool as long as the device itself is relatively expensive in respect to the concentrator. One device with a concentrator can put out 10 times to 100 times the power with little additional cost, especially if the concentrator is incorporated into the system structure and package. Another key factor is the type or characteristic of the system being considered. The total solar home, for instance, takes advantage of the thermal heat generated as well as the electrical output, thus providing more benefit than an electrical system only. The SSPS system has a ten to one advantage of sunlight availability, because of no nighttime, no atmosphere attenuation, no dust, no clouds, etc., but it has the disadvantages of transportation to space and beaming back the power. Probably the most important key factor in cost reduction is the mass production impact. Mass production is needed to obtain the experience and move down the learning curve.

Now let us consider the device fabrication process in more detail. The goals we have been working on in this area are shown in Fig. 4. Larger area cells are being built using simplified processes. Higher rate processes are being used. Machines are being used to transfer and handle the devices much faster. Yields are being increased because the process is less complicated and because the tolerances and specifications for terrestrial cells can be much more relaxed than space cells. Efficiencies of production-type cells have recently increased to over 14 percent AMO (16.5 percent AMI) and are expected to increase still further. Material and power utilization has been decreased as a result of the elimination of steps and by replacing with less expensive materials.



As a result of the above work and following an R&D program similar to that described, it is believed that the milestone schedule shown in Fig. 5 can be achieved. We are confident that photovoltaic power system costs can be reduced below \$5/watt by 1978 and below \$1/watt by 1983. The production rate should be able to be increased to 6 MW/year by 1978 and 200 MW/year by 1983 based on the assumption that capacity can be doubled each year for the next 10 years. Meeting these milestones would put photovoltaic power systems into a highly promising position for being selected for a large-scale demonstration program in the mid-1980's.

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3. Ralph, E. L., "Large Scale Solar Electric Power Generation," *Journal of Solar Energy*, Vol. 14, No. 1, 1972.
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### Discussion

Q: Has anybody ever made a solar cell using ion implantation?

A: Yes.

Q: Does it work as well?

A: It makes a good cell. You can use that technique, if it has some advantage. I don't know of any cost advantage of doing that, but certainly from a process standpoint you can make a good cell that way. It has been done.

Q: You meant \$20.00/watt if you go into mass production?

A: No, that's today on a large order.

Q: This \$5.00 per watt per cell is in volume, I take it?

A: This is on a quantity buy today.

Q: What do you mean a quantity?

A: Twenty-cm<sup>2</sup>-type cells - not a 4-cm<sup>2</sup>-type cell.

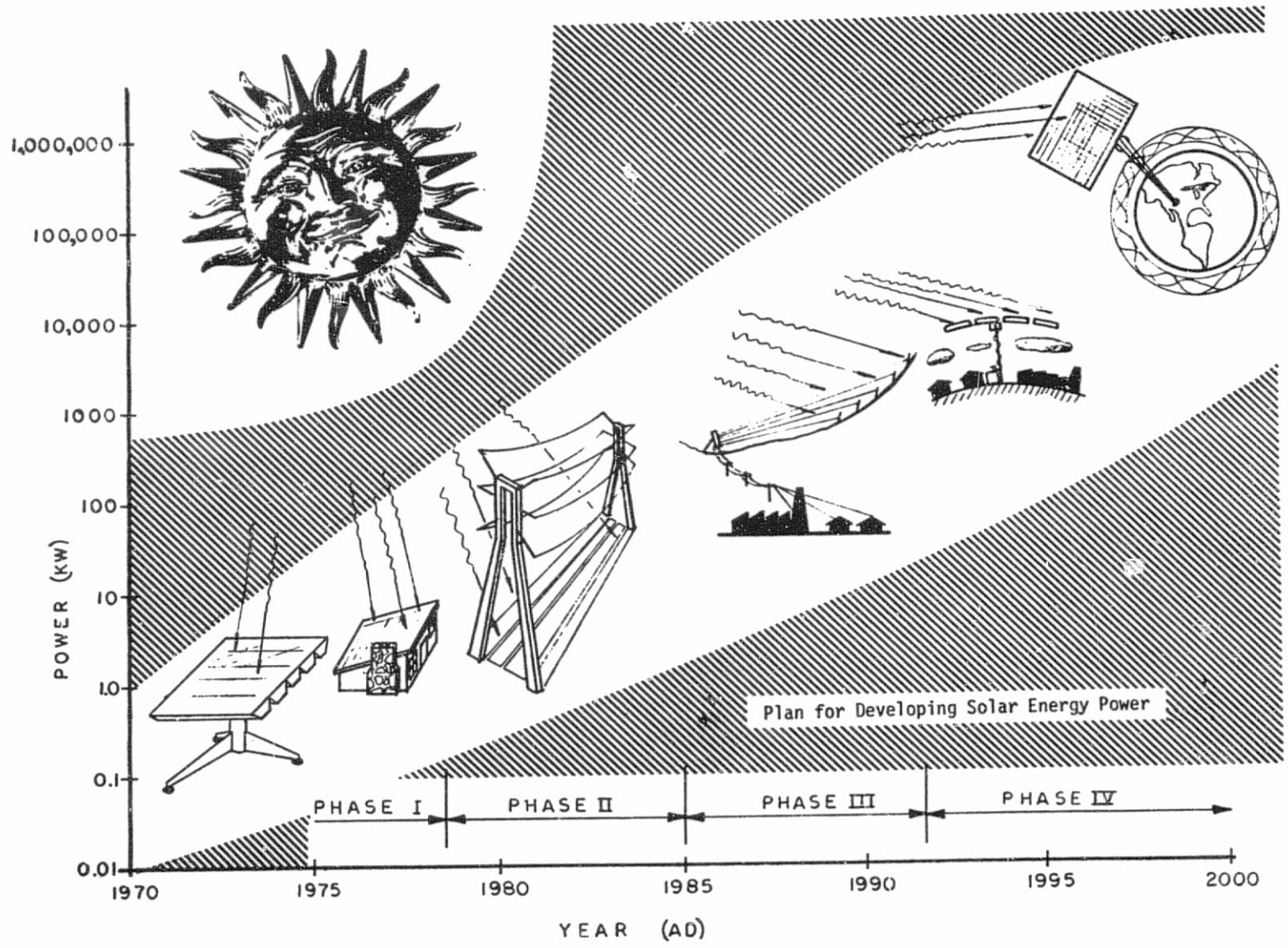


Fig. 1

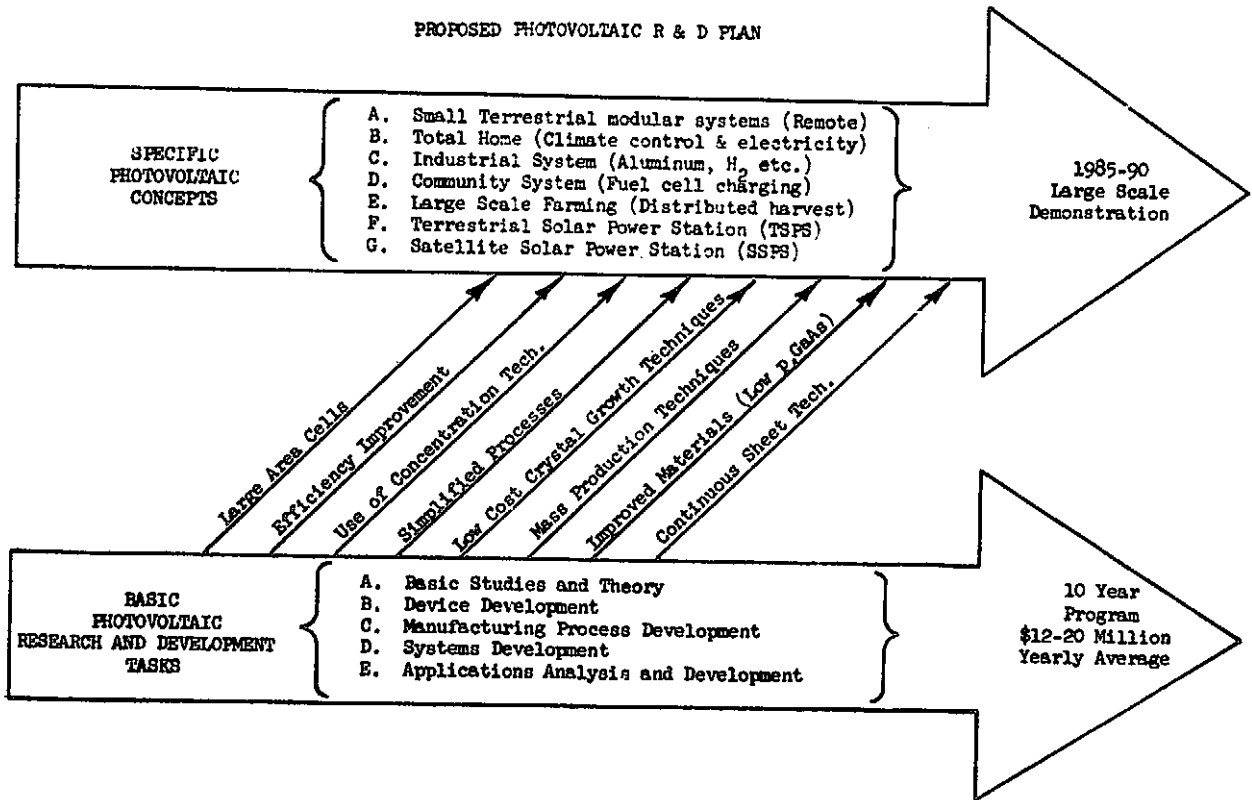


Fig. 2

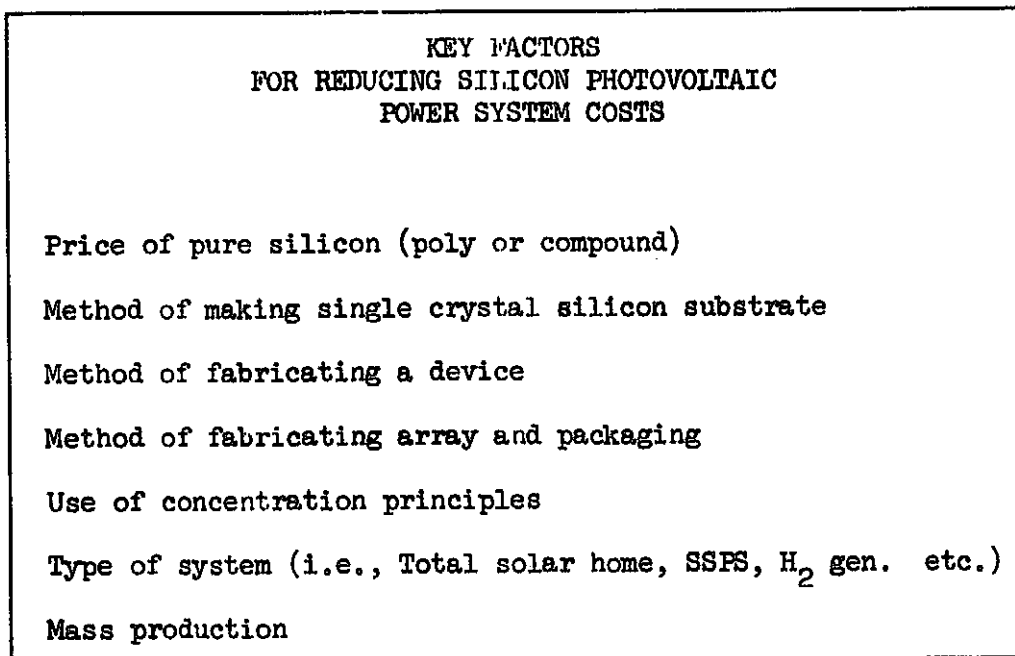


Fig. 3

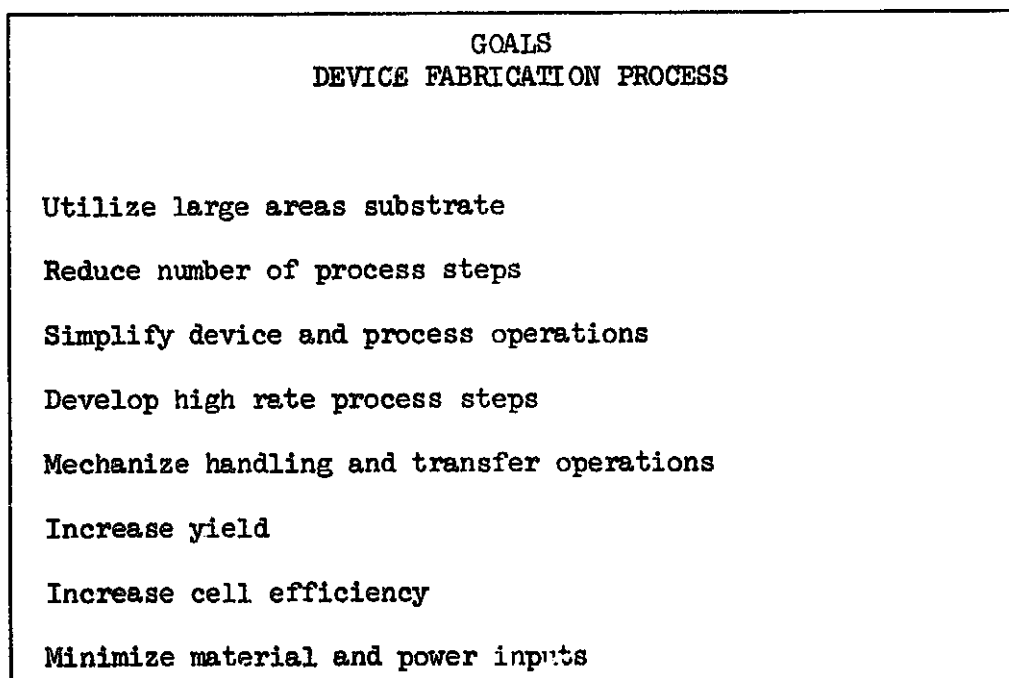


Fig. 4

MILESTONE SCHEDULE			
PARAMETER	TECHNOLOGY STATUS		
	PRESENT 1973	5 YEARS 1978	10 YEARS 1983
Cell Size (cm <sup>2</sup> )	20	45 or Cont. Ribbon	Continuous Multi-Ribbon or sheet
Cell Efficiency (% AMO)	14	16	18
(% AMI)	16.5	19	21
Cell Cost (\$/watt AMI)	5	2.50	0.30
Power System Cost (\$/watt AMI)	20	5	<1
Production Rate (Mw/yr)	.09	6	200

Fig. 5.

## SILICON CELLS

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### Presentation Summary

The cost of silicon solar cells, and therefore the cost of terrestrial solar electric energy, is controlled by the space market. This reference is somewhat unfortunate since the space requirements are different from the terrestrial situation. I believe that efficient terrestrial cells could be produced now for about \$10/W(peak) and a terrestrial panel could be completed for approximately \$20/W(peak). At the moment, however, there is no industrial base to support these prices. We hope that through Solarex these costs, and maybe lower levels, could be tested. It is essential to find a sufficient "specialty" market to support such prices. The price can be reduced further by concentration, but again, the market must expand faster than the cost reduction involved.

At a few dollars per watt level the cost of silicon becomes the dominant factor. Assuming that the cost of silicon will not decrease abruptly, continued cost reduction could be continued by using less silicon. Transistors and integrated circuits became less expensive by increasing the device density; since in solar energy conversion we need the area, the thickness must be decreased. We believe that thin silicon, supported by an inexpensive base is an important promise for the future. The violet cell work has shown that the terrestrial efficiency can be increased to 18 percent in a 10-mil silicon slice. Looking into the thickness dependence further we find that the conversion efficiency changes slowly with thickness, as expected. A calculation was made to match a theoretical curve with these measured points to predict the thickness dependence. The curve predicts that it should be possible to obtain over 10 percent conversion efficiency with a 10-micron silicon layer. Of course, this thin film should be nearly single crystal.

We also believe that the terrestrial conversion efficiency should be increased further. It seems certain that the efficiency could be raised over 20 percent. An effort in this direction will maintain a scientific/technical excellence, and the factors involved in the improvement will be applicable to thin film work also. The short wavelength response, the sharpness of the diode, the photovoltage are all factors determined by the first few thousand angstroms of silicon at the surface.

At this point there are real hopes for the development of inexpensive silicon cells.

### Discussion

- Q: What are your specifications on silicon with respect to resistivity, lifetime, and mobility to make an 18 percent cell?
- A: That's partially COMSAT work.
- Q: What do you think the incoming specifications should be?
- A: At about 2 ohm-cm, the current of the bulk is just starting to fall off and the top layer is just starting to take over. So, at 2 ohm-cm, you can obtain roughly 18 percent.
- Q: Are there any requirements on lifetime or mobility?
- A: For mobility, I don't think very much; for lifetime, maybe.
- Q: What of mechanical perfection? Do you have any other requirement besides 2 ohm-cm?

SESSION I. SINGLE-CRYSTAL SILICON - LINDMAYER

- A: Obviously it has to be a good crystal, because an 18 percent cell with red response in it is a significant factor.
- Q: What are the requirements?
- A: About 30 to 40 microseconds, and that's all that is needed.
- Q: When you are making these efficiency projections, are you really assuming AM1 spectra and not AMO, since you are relying so much on improvements in surface effects?
- A: Yes, the 18 percent is with the air mass between one and two on the ground, of course, and the 20 percent efficiency will be achieved, I am sure, on the ground.
- Q: With a 10-micron cell do you think it is reasonable to expect 10 percent? AM1 spectrum?
- A: Yes, I think so. If one does have 20 percent efficiency to start with, ten of it is really coming from the first few thousand angstroms of the silicon. Say 10,000 angstroms or 20,000 angstroms of the top layer and that's the part we can hang on to when we go down to very thin films of silicon.
- Q: Theoretically, what lifetime is desired today in silicon 2 ohm-cm?
- A: It is 30, 40, or 100 microseconds for a 10-mil slice, because we are then counting on the red response when we are saying 20 percent; but as we go closer to the junction, because of the shorter wavelength and the penetration factor, the lifetime becomes less and less important.
- Q: Concerning surface properties (because we are interested in a very shallow junction) what is the lifetime near the surface?
- A: In the violet cell, we have the band bent all the way to the surface, and there is no more dead layer. Thus, there is a built-in field reaching up to the very surface. If there is a very high built-in field, a blue carrier is immediately brought up to saturation velocity and is driven away from the surface. So you can argue that there really is no lifetime limitation nor is there truly a surface recombination limitation on the short wavelength response.
- Q: Would you expect to be able to get such cells on epitaxially grown silicon? Have you tried that?
- A: You mean 20 percent cells? 18 percent cells? No, I don't think so.
- Q: Why not?
- A: It depends on the quality. Because you are giving up maybe some of the red response, unless the epitaxial layer is really of such good quality.
- Q: Did you say 10 percent would be available from a 10-micron-thick layer on the surface of the earth?
- A: Yes.
- Q: On the surface of the earth - not in space?
- A: Right.
- Q: Air mass one?
- A: Right.

## FIVE YEARS OF SILICON WEB CRYSTAL GROWTH

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### Presentation Summary

Experience in growing<sup>2</sup> more than 2000 meters of silicon dendritic web crystal (Ref. 1) in the mid-1960's provides a guide to current efforts to grow low cost sheets of silicon. This experience can be valuable to the future development of dendritic growth as well as other sheet growth processes, such as EFG (Ref. 2).

This extensive growth of silicon web crystal was from 5°C super cooled 40 gram melts of silicon in round, non-rotated quartz crucibles. The crystals were extracted through an exit tube at the top of the furnace and wound on a 90-cm-diameter reel. The 10-kw, 450-kHz induction heating generator was controlled using an infrared sensor focused on the molybdenum susceptor. Nominal widths from 8 to 15 mm and lengths to about 10 meters were achieved.

Of potential value to all future attempts to grow low cost sheets of silicon are the observations that:

1. Silicon sheet 0.05 to 0.3 mm thick must be reinforced (such as by dendrites) or uniformly supported mechanically to be handled without major danger of breakages.
2. A continuous process is essential to achieve sufficiently low cost for large application for photovoltaic cells.
3. A reel-type pull system is superior to fully linear systems for pulling the sheet crystal from the furnace.
4. A set of twin planes in the sheet significantly aids the growth process.

A feasibility study showed appreciable potential for a continuous web crystal growth process. For this series of experiments, a linear quartz crucible was directly heated by a mating graphite (resistance) heater. This furnace system produced an improved thermal geometry, had superior response time for the temperature control, and used much less energy and capital. By maintaining a hotter region at one end of the linear crucible, it was believed silicon could be added to the melt during crystal growth, which is necessary for a continuous growth process.

The dendritic web growth process may permit the growth of sheet silicon suitable for large area photovoltaic cells at a crystal cost less than 1.0¢/cm<sup>2</sup> if:

1. The thermal geometry in the melt can be controlled for growing web crystal 5 cm wide.
2. The growth process is sufficiently continuous so that a majority of the operating time is used for growing uniform crystal.

---

<sup>1</sup>Present address: Dow Corning Ltd.  
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<sup>2</sup>Under license from Westinghouse.



3. Full automatic process control is used, such as by use of an infrared video sensor focused on the freezing interface and directly coupled via suitable programming to control the melt temperature and pull system with millisecond response time.

This is believed to be achievable.

### References

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2. Ciszek, T. F., "Edge-Defined, Film-Fed Growth (EFG) of Silicon Ribbons," *Mat. Res. Bull.* Vol. 7, pp. 731-738, 1972.

### Discussion

Q: What was the approximate speed of growth?

A: Most of it was grown about 2 centimeters a minute. I believe with full automatic control, you should be able to extend that somewhat.

Q: The dendrites you say would remain in place. What percentage of the total weight would be in the dendrite, since that is going to be wasted silicon? I don't believe you can make a cell out of that material. In other words, that dendrite material itself will not make a good cell.

A: I don't think it would be practical to make a cell out of the dendrite. I believe there was some initial work to make cells out of the dendrites themselves, but as the width increases, I would expect that the dendrites would be basically there only for the support, and should be less than a quarter of the weight. This still would be a significant portion of the mass. It all depends upon the widths that one can achieve and it seems that 5 centimeters width should be achievable.

Q: Have you counted the dislocation density or measured the lifetime in your material?

A: As was indicated earlier, lifetime measurement of very thin pieces of silicon is a rather difficult measurement task. Dislocation densities would vary from a very gross amount, which became an ideal tool for aligning SOT land cameras, and there were very many of these results published, but also, it has been shown that you could grow dislocation-free. Dislocations would tend to line up with the twin plane and would be near the twin-plane region. I believe the dislocation probably affected the lifetime or was probably the major contributor to the lifetime, which was believed to be in the one to ten microsecond region, but no direct measurements were able to be made.

Q: Has anyone ever demonstrated that there is a relation between dislocation content and lifetime?

A: There have been a number of papers related to float-zone silicon showing that there is quite a definite relationship between dislocation density and lifetime. This is normally, though, at much higher dislocation densities upwards of 1,000 to 100,000 to a million per square centimeter.

C: There is a very elegant way of measuring the lifetime in thin silicon layers using the MOS capacitance technique. We have measured the lifetime recently on webs, but it was not too good as these webs were pretty old material. They could be considerably improved.

## A THEORETICAL ANALYSIS OF THE EFG GROWTH OF SILICON RIBBONS

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### Presentation Summary

#### Introduction

A most critical area of concern in any crystal growth process is the shape of the interface between the growing crystal and the parent phase, and the stability of the interface to changes in the process variables. This problem is particularly important in the EFG process (Refs. 1 and 2), a technique which has been developed for the growth of crystals with controlled geometries. As described by Dr. Mlavsky in the preceding paper (Ref. 3), the aim of the present research is to adapt the EFG process to the continuous growth of single-crystal silicon ribbons from the melt. This requires a thorough understanding of the factors which influence the interface shape and stability.

In the EFG growth of silicon ribbons, the problems associated with the solid-liquid interface require the theoretical understanding of three basic physical processes: (1) the problem of the heat flow in the ribbon-shaped geometry; (2) the problem of the fluid flow and the associated problems of the static and dynamic stability of the meniscus film; and (3) the effects of wetting or contact angle between the liquid silicon and the die surface on the stability of the growth process.

Because of the very nature of the EFG technique, it is imperative that the theoretical analyses should closely correspond to the experimental crystal growth setup and conditions. In this way, the analyses are not only expected to provide an understanding (and explanation) of the experimentally observed behavior, but also to suggest possible improvements in the design and development of the crystal growth equipment. We see, in fact, that the physical processes described above relate directly to a number of experimental design variables. The analysis of the heat flow, for example, relates to the problem of the furnace and the die design. The die design is also affected by considerations of the fluid flow and the problem of the contact angle. The latter process also plays the dominant role in the selection of the die material.

The ultimate aim of the theoretical analyses is to provide a parametric description of the stability of the EFG process in terms of the system and process variables. It is therefore useful at this juncture to digress on what we mean by the "stability" of the EFG process.

On a macroscopic level, stable growth is indicated by the uniformity of the geometrical dimensions of the crystal. This is the ultimate measure of the stability of the process, and the continuous maintenance of such stable growth is the ultimate requirement for useful silicon ribbons to be produced by this technique.

On a more fundamental level, we are concerned with two particular aspects of the EFG process: (1) the static stability of the meniscus film; and (2) the thermal stability of the solid-liquid interface. The basic requirement for stability in either case is that any departure from equilibrium or steady-state conditions should be followed by a return to these conditions. In other words, the system should be self-stabilizing with respect to fluctuations in the process variables. With this in mind, and the fact that the actual crystal growth process unavoidably involves fluctuations in the process variables, such as the heat input or the crystal pull rate, we can define our interest in the stability of the EFG process as follows: we seek the range of permissible fluctuations in the process variables for which continuous growth can persist.

In this paper, we examine the theoretical basis for the "edge-definition" in the EFG of silicon ribbons; i.e., we investigate the relationship of the crystal geometry (such as the ribbon thickness) to the system and the growth parameters. This is clearly the fundamental theoretical problem in the EFG process; the models used here also form the basis for the treatment of the stability problems described above. The theoretical analysis is then applied to some experimental data leading to suggested improvements in the crystal growth setup.

### The Edge-Definition in the EFG of Silicon Ribbons

To begin a description of the theoretical analysis, it is useful to identify the independent and dependent variables in the model of the EFG process (Fig. 1). The independent (or process) variables are those which can be selected in the experiments, and they are: the die thickness ( $t_d$ ), the die width ( $w_d$ ), the pull rate imposed on the crystal ( $V_p$ ), some measure of the heat input into the system ( $\Delta T$ )<sup>1</sup>, the effective height ( $h_{eff}$ ) of the solid-liquid interface above the liquid level in the crucible, and the contact angle ( $\phi_d$ ) between the liquid silicon and the die surface.

The dependent variables of the process are those which the system selects in either a transient or a steady-state manner, and they are: the ribbon thickness ( $t$ ), the ribbon width ( $w$ ), the meniscus thickness ( $s$ ), the rate of advance of the solid-liquid interface ( $V_g$ ), and the angle ( $\phi_0$ ) between the vertical axis and the meniscus at the solid-liquid interface (Fig. 1).

For our present purposes, we assume that  $w \approx w_d = \text{constant} \gg t$  and that the contact angle requirement ( $\phi_d$ ) can be satisfied at the outer edge of the die. The problem of the edge-definition is to find a theoretical relationship between  $t$  and the other system variables at steady state, i.e.,

$$t = f(t_d, h_{eff}, V_p = V_g, \Delta T, s, \phi_0) \quad (1)$$

One such relationship is obtained by considering the shape of the meniscus in Fig. 1 as determined by the hydrostatic pressure difference ( $\Delta p$ ) across a point on the meniscus and by the interfacial free energy ( $\gamma$ ). To a very good approximation, the radius of curvature of the meniscus is constant, and is given by  $R_1 = \gamma/\Delta p = \gamma/\rho g h_{eff}$ , where  $\rho$  is the density of liquid Si and  $g$  is the gravitational constant. Here the term  $h_{eff}$  includes the viscous pressure drops associated with the flow of liquid silicon through the capillary in the die and with the flow in the film on top of the die. The analysis gives the ribbon thickness in implicit form, viz.,

$$\phi_0 = \tan^{-1} \left[ \frac{t_d - t}{2s} \right] \cdot \pi/2 + \cos^{-1} \left[ \frac{y}{2R_1} \right] \quad (2)$$

where

$$y = [s^2 + (t_d - t)^2/4]^{1/2}$$

A schematic illustration of the dependence of  $t$  on  $s$  and  $\phi_0$  is shown in Fig. 2.

Another independent relationship is obtained from the consideration of the steady-state heat balance at the solid-liquid interface. At steady state, the heat ( $Q_R$ ) removed from the interface by conduction-radiation through the ribbon must be balanced by the heat ( $Q_L$ ) generated at the solid-liquid interface by the process of solidification, plus the heat ( $Q_M$ ) arriving at the interface by conduction across the meniscus film, i.e.,  $Q_R = Q_L + Q_M$ .

$$t = \frac{2}{3} k_m \sigma \epsilon T_m^5 / [\rho_s V_g L + k_l \Delta T/s]^2 \quad (3)$$

<sup>1</sup>Here we consider  $\Delta T = T_d - T_m$ , where  $T_d$  is the temperature at the top of the die surface and  $T_m$  is the melting temperature of Si.

where the various terms are described below.<sup>2</sup> From the schematic in Fig. 3, we see that the ribbon thickness decreases as either the growth rate or the heat input into the system increases. This result agrees with the experimentally observed behaviour.

From a consideration of Figs. 2 and 3, we see that the problem of the edge-definition is not uniquely resolved by the simultaneous solution of Eqs. (2) and (3): we must also specify the independent variable  $\phi_0$  in order to completely characterize the system. There is no data available at this time, however, regarding the value of  $\phi_0$  which is consistent with crystal growth with a uniform cross-section (other than the intuitive guess that  $\phi_0 \sim 0^\circ$ ). Experimental work on suitable model systems is now being considered in order to gain some insight into this problem.

#### Analysis of Dumbbell-Shaped Ribbon

The above analysis can be used to explain a number of experimental observations, and also to suggest possible changes or improvements in the experimental setup. Many of the ribbons which were grown to date, for example, were observed to have a dumbbell-shaped cross-section: the data (Ref. 4) obtained in two specific experiments is shown in Fig. 4. In addition to the variation of the ribbon thickness, it was observed that the meniscus thickness and the die temperature decreased from the center to the ends of the ribbon ( $s \approx 0.0125$  cm,  $\Delta T \sim 5$  to  $7^\circ\text{C}$  near the center;  $s \approx 0.0075$  cm,  $\Delta T \sim 3$  to  $5^\circ\text{C}$  near the ends). Substituting the observed growth rates of  $0.0282$  cm/sec and  $0.0169$  cm/sec into the heat-flow model of Eq. (3), we obtain the  $t$ - $s$  relationships shown in Figs. 5 and 6, respectively. As indicated by the broken lines in these figures, there is good quantitative agreement between the model of Eq. (3) and the experimentally reported values of the variables.

In order to explain the dumbbell-shaped cross-section, we have to combine Figs. 5 and 6 with the  $t$ - $s$  curves given by the hydrostatic considerations of Eq. (2). The latter curves are shown in Fig. 7 as a function of the angle  $\phi_0$ ; these results are approximately independent of the value of the die thickness ( $t_d = 0.05$  to  $0.06$  cm in the experiments; the exact value is somewhat uncertain). It is reasonable to assume now that the value of  $\phi_0$  is constant in a given experiment; combining Figs. 5 and 7 (or 6 and 7), we therefore see that the dumbbell shape can be explained by the intersection of a  $\phi_0 = \text{constant}$  ( $\sim 30^\circ$  to  $40^\circ$ ) contour with the appropriate  $\Delta T$  curves in Fig. 5 (or Fig. 6). Although the above value of  $\phi_0$  is seemingly large for steady-state growth with a uniform cross-section, it is consistent with the result that the radius of curvature of the meniscus  $R_1 \gg s$  and that  $t$  is approximately  $1/2$  to  $2/3$  of the die thickness.

Finally, the above results suggest a way in which the experimental setup can be modified in order to obtain a ribbon with  $t = \text{constant}$  along its entire width: specifically, the die thickness can be varied from the center to the ends of the die. However, it may be more desirable to keep the die thickness constant, and rather to change the thermal environment such as to obtain a uniform temperature along the entire die surface.

#### Conclusions

We have attempted to demonstrate in this paper that: (1) the EFG process is amenable to a detailed theoretical description and analysis; (2) a close correspondence can be achieved between theory and crystal growth experiments which can not only guide further theory, but also to suggest changes and improvements in the experimental setup; and (3) based on the impact of the theoretical analyses on the experimental program thus far, we can expect to achieve full exploitation of the potentials of the EFG technique. In other words, the crystal growth rates which are required from the point of view of economy are consistent with the steady-state growth rates obtained from the theoretical models.

Finally, the present calculations form the necessary background for further theoretical work on problems such as the transient spreading of the ribbon in the width-dimension, and the description of the stability of the EFG process. The models can also be used to extend the EFG theory to the case of nonwetting and partially wetting dies. Problems of the interface shape and stability, and the effects of solute distribution on the crystallization process also require further theoretical work.

<sup>2</sup>In Eq. (3),  $\sigma$  is the Stefan-Boltzmann constant,  $a/e$  is the emissivity,  $k_m$  is the thermal conductivity of solid Si at the melting temperature,  $k_l$  is the thermal conductivity of liquid Si,  $L$  is the latent heat of fusion in ergs/gm, and  $\rho_s$  is the density of solid Si.

### Acknowledgements

This research was supported in part by the National Science Foundation, Research Applied to National Needs, under Grant No. GI-37067X and the Division of Engineering and Applied Physics, Harvard University. The authors are grateful to H. E. Bates, D. N. Jewett, A. I. Mlavsky and J. C. Swartz of Tyco Laboratories for illuminating discussions.

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3. Mlavsky, A. I., in these Proceedings.
4. Data supplied by Tyco Laboratories.

### Discussion

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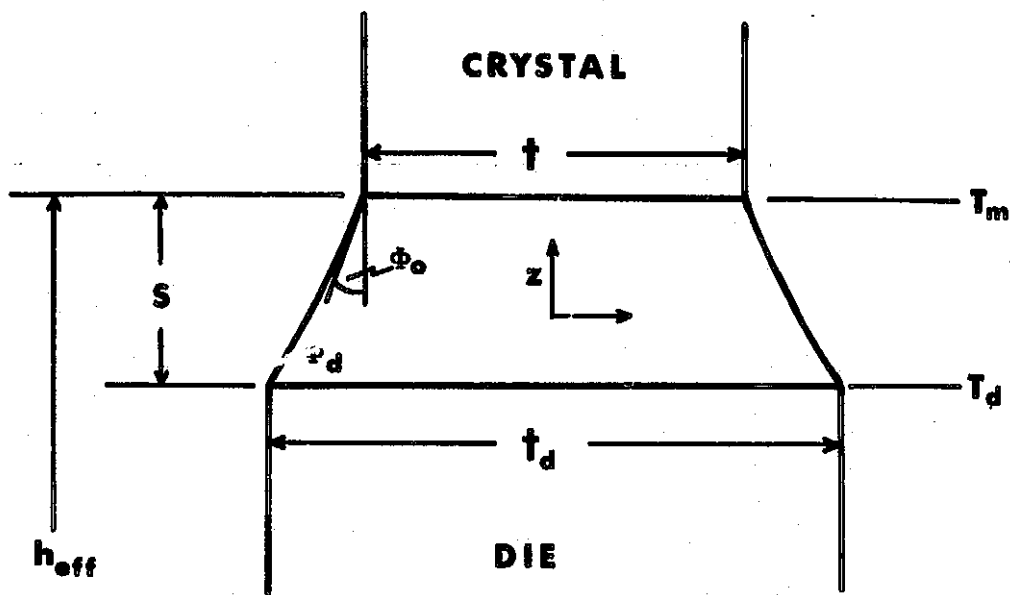


Fig. 1. Schematic Cross-Section of EFG Ribbon Showing the Variables in the Theoretical Analysis

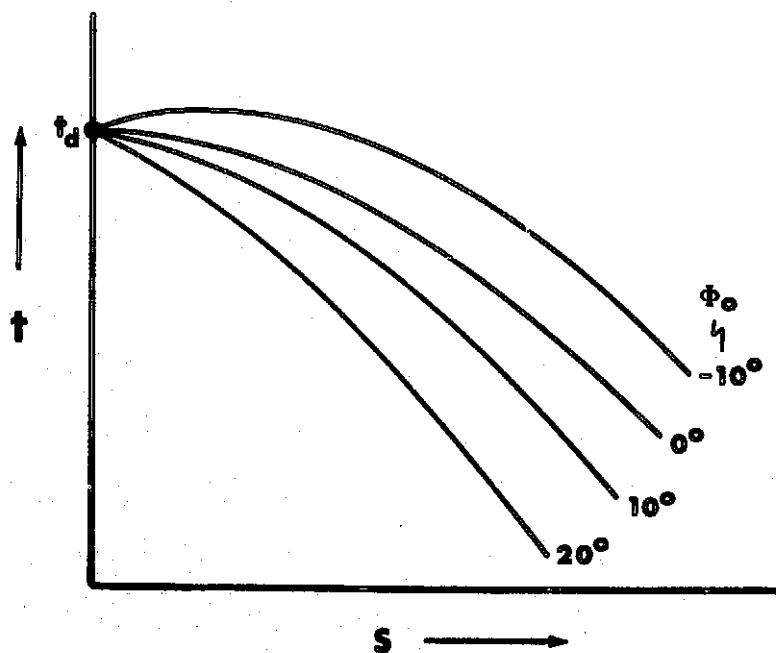


Fig. 2. The Variation of Ribbon Thickness with Meniscus Thickness and  $\phi_0$  Based on Hydrostatic Considerations

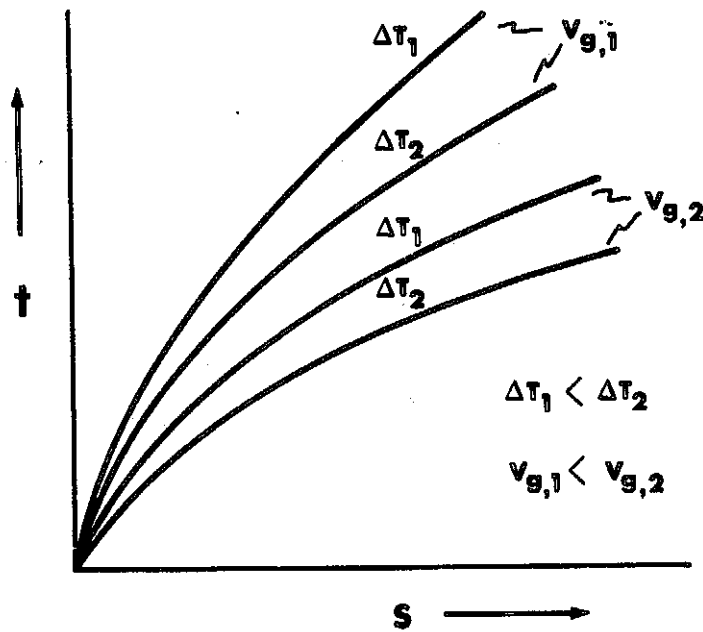


Fig. 3. The Variation of Ribbon Thickness with Meniscus Thickness,  $V_g$  and  $\Delta T$  Based on Steady-State Heat Flow at the Solid-Liquid Interface

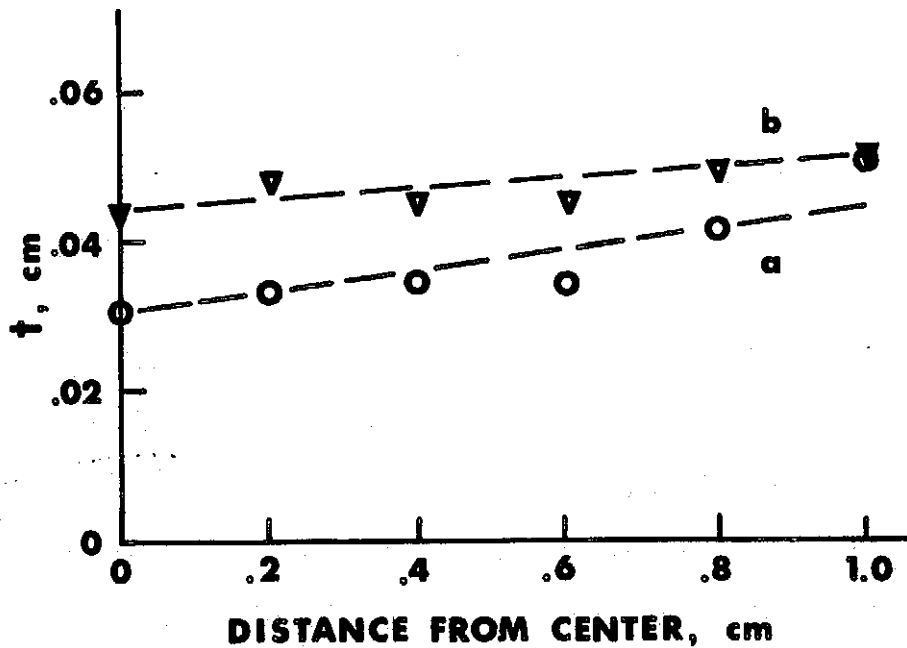


Fig. 4. Experimental Data for the Variation of  $t$  with Distance from the Center of the Ribbon ( $h_{eff} \approx 1.5$  cm,  $w \approx 2$  cm,  $V_g = 0.0282$  cm/sec (Curve a) and 0.0169 cm/sec (Curve b))

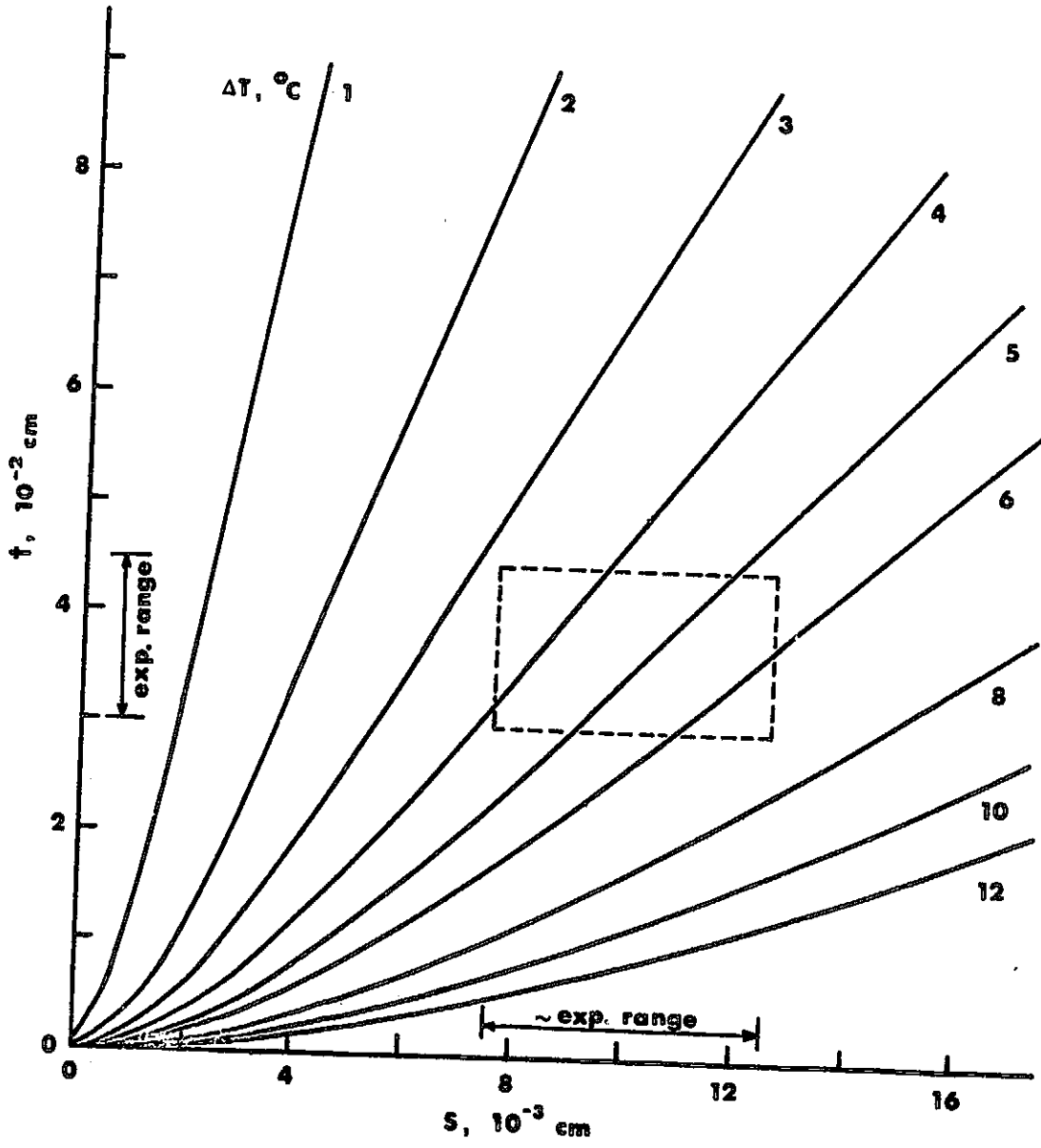


Fig. 5. Theoretical  $t$ - $s$  Curves (Eq. (3)) as a Function of  $\Delta T$  for Case a in Fig. 4



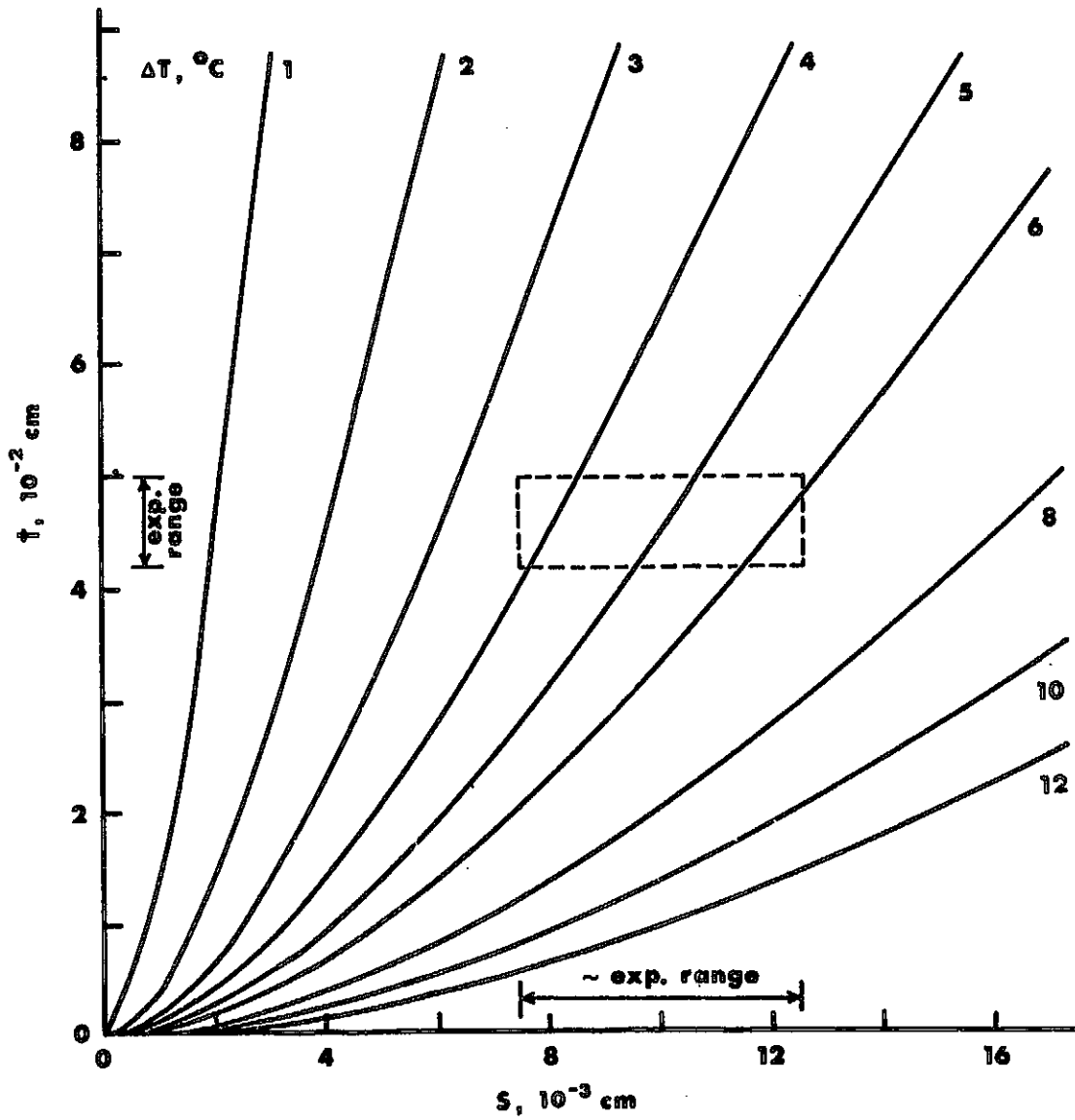


Fig. 6. Theoretical  $t$ - $s$  Curves (Eq. (3)) as a Function of  $\Delta T$  for Case b in Fig. 4

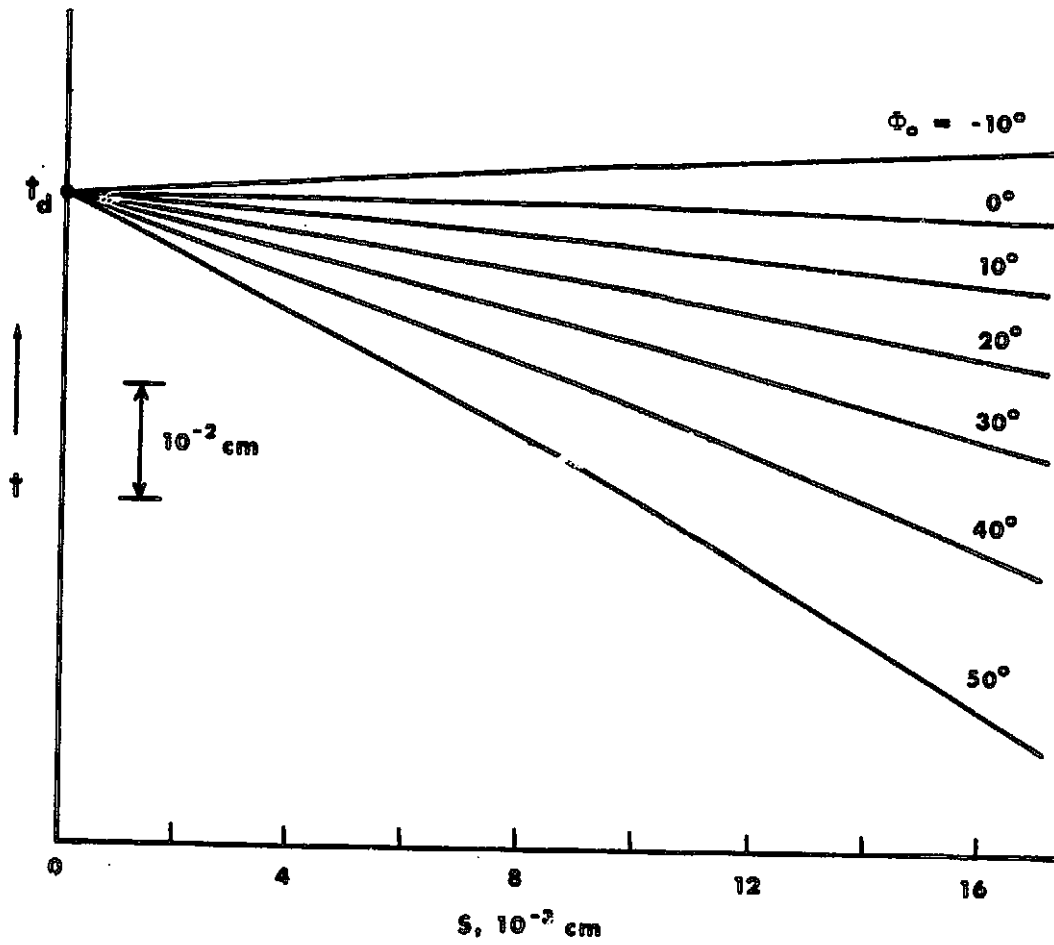


Fig. 7. Theoretical  $t$ - $s$  Curves (Eq. (2)) as a Function of  $\phi_0$  for the Data in Fig. 4

## THE EFG GROWTH OF SILICON RIBBON FOR SOLAR CELLS

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### Presentation Summary

EFG ("edge-defined, film-fed growth") is a technique for the continuous production of controlled profile single crystals from the melt (Refs. 1, 2, 3, 4, 5). The molten phase of the material to be grown rises by capillarity to the top of an opening in an orifice or die located in the crucible. When the temperature is correctly adjusted, a seed crystal introduced into the melt in the die begins to grow. As the seed is withdrawn, the melt spreads across the top surface of the die, stopping at any vertical plane. The growing crystal then has a cross section governed entirely by the shape of the film. For example, for the growth of a ribbon, the die consists of two plates separated by a planar capillary channel (Fig. 1); as shown, the dimensions of the growing ribbon are governed by the *outside* edges of the die.

The features of EFG which distinguish it clearly from all other growth techniques are listed in Fig. 2. All of these advantages have been proven in the industrial manufacture of sapphire shapes, some of which are shown in Fig. 3.

The application of EFG to the growth of silicon ribbon for solar cells poses certain special problems. Thus, a die material is required which is wet by molten silicon, but does not introduce deleterious impurities into the solid. Problems specific to silicon are listed in Fig. 4.

Under programs with NSF (Harvard), Jet Propulsion Laboratory, and Tyco, we have grown many silicon ribbons, some of which are shown in Fig. 5, and the properties of which are shown in Fig. 6. In brief, the basic feasibility of the application of EFG to the growth of silicon ribbon has been demonstrated, although clearly much remains to be done to improve the reproducibility of the process and the quality of the silicon.

A cost projection has been made based on scaling up the process to continuous ribbon growth, and to the growth of multiple continuous ribbons with continuous melt replenishment. This data is summarized in Fig. 7. A cost projection has also been made by others (Ref. 6), leading to an estimate of \$375/kw for solar cells made using EFG ribbon, based on a raw silicon cost of \$35/kg.

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### Discussion

- Q: What does that mean in yield of solar cells? What assumption was made for the solar cell yield from the ribbon, and are you just talking about ribbon costs?
- A: Yes, ribbon, but what I am using is some numbers which were generated by a group of people, most of whom are here today: Currin, Ling, Ralph, Dr. Stim, who published a paper at the last Photovoltaic Specialists Conference in which they assumed that the EFG ribbon was available. They computed the cost of the solar cells and I have simply taken their incremental costs going from the ribbon to the solar cell and assumed they are right. That would add about \$7.00 a pound to this cost, which will give you \$30.00 a pound. And since you get 200 watts from a pound of four-mil-thick silicon solar cells at ten percent efficiency, that equates to about \$150.00 a kilowatt.
- Q: Can you say what the maximum lifetime is that you have obtained from a silicon ribbon?
- A: No, I can't, I'm afraid. It is very difficult to measure lifetime in things which have a lot of grain boundaries. We are now measuring lifetime, but we don't have that ready yet. We are also, incidentally, making solar cells out of this material, having set up in great haste to make an amount of ribbon material, which we can now do with some efficiency.
- Q: Figure 1 shows some efficiencies as a function of the yield, and there was an efficiency of about 15 percent. At what power level was that?
- A: What power level? That was a solar cell that was normally four square centimeters; it produced something on the order of around 75-76 milliwatts. Is that what you mean?
- Q: A device?
- A: A device, yes -- a device that produced about 76 milliwatts out of four square centimeters.
- Q: Well actually, it is only in the milliwatt range for this cell?
- A: Yes, for this cell.
- Q: What crucible materials have you tried that worked out best -- I mean die materials?
- A: Die materials? There are two basic die materials which we have worked with. Quartz reacts least among materials that are allowed to come into contact with molten silicon and carbon. Quartz has a problem in that it doesn't like to be wetted by molten silicon and it needs to be induced to do so. But quartz has been made to work in various shapes and forms.
- Q: What about silicon carbide?
- A: Silicon carbide has also been used and this has some fair promise. You have a thermodynamic problem and you have a kinetic problem. I think, in fact, all you ever have is a kinetic problem, since there is always reactivity at high temperatures, and the rate of dissolution of silicon carbide is very low, indeed.

Q: How does the EFG process differ from the well-known dendritic growth process that was worked on quite a few years ago?

A: There are almost no similarities. This is not a dendritic process. The growth interface is smooth, the temperature is positive in the liquid with respect to the growth interface, and so the active interface is more like Czochralsky than dendritic. By varying the temperature, the EFG process will permit one to grow the planar interface, the cellular interface, or the dendritic interface. Because it is not a dendritic process, one can grow in any crystallographic orientation. One can grow a single crystal which has no inherent twin structure. The third and most important respect, I think, is that you can grow any shape you like, and I refer you to the slide on the sapphire shapes. You can, in fact, grow a crystal of any shape which is determined by the die, not by the crystallography and by the temperature distribution in the melt. So it is possible to grow filaments as I have shown. You can grow the filaments in the dendritic regime by growing from a supercooled film, but you can also grow the planar interface and get high quality single crystals.

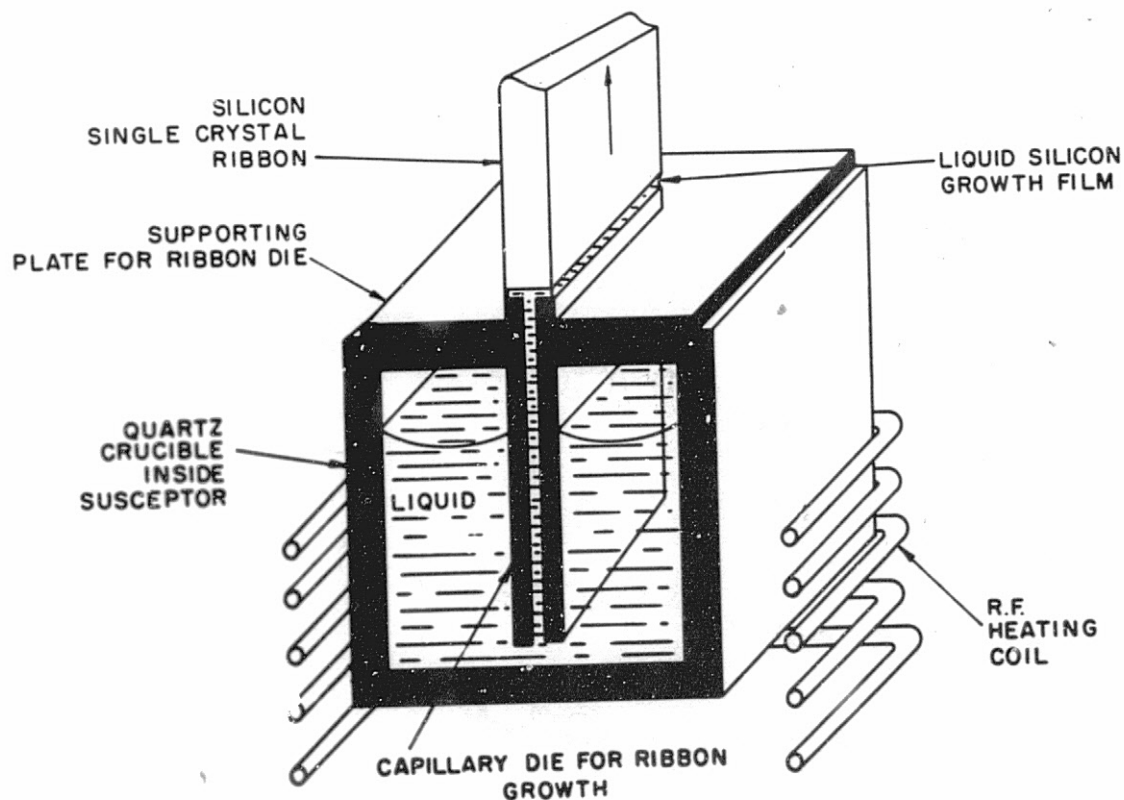


Fig. 1. Capillary Die for Ribbon Growth

REQUIREMENTS	FEATURES
<ul style="list-style-type: none"> <li>● NON-VOLATILE STABLE MELT</li> <li>● NON-REACTIVE CRUCIBLE</li> <li>● NON-REACTIVE BUT WETTING (AT LEAST PARTIALLY) "DIE"</li> </ul>	<ul style="list-style-type: none"> <li>● DIRECT PRODUCTION TO (VIRTUALLY) ANY SHAPE</li> <li>● FAST GROWTH RATES</li> <li>● SELF-STABILIZING GROWTH</li> <li>● MULTIPLE PRODUCT FROM ONE CRUCIBLE</li> <li>● CONTINUOUS MELT REPLENISHMENT</li> </ul>

Fig. 2. Edge-Defined, Film-Fed Growth (EFG)  
Summary of Requirements and Features

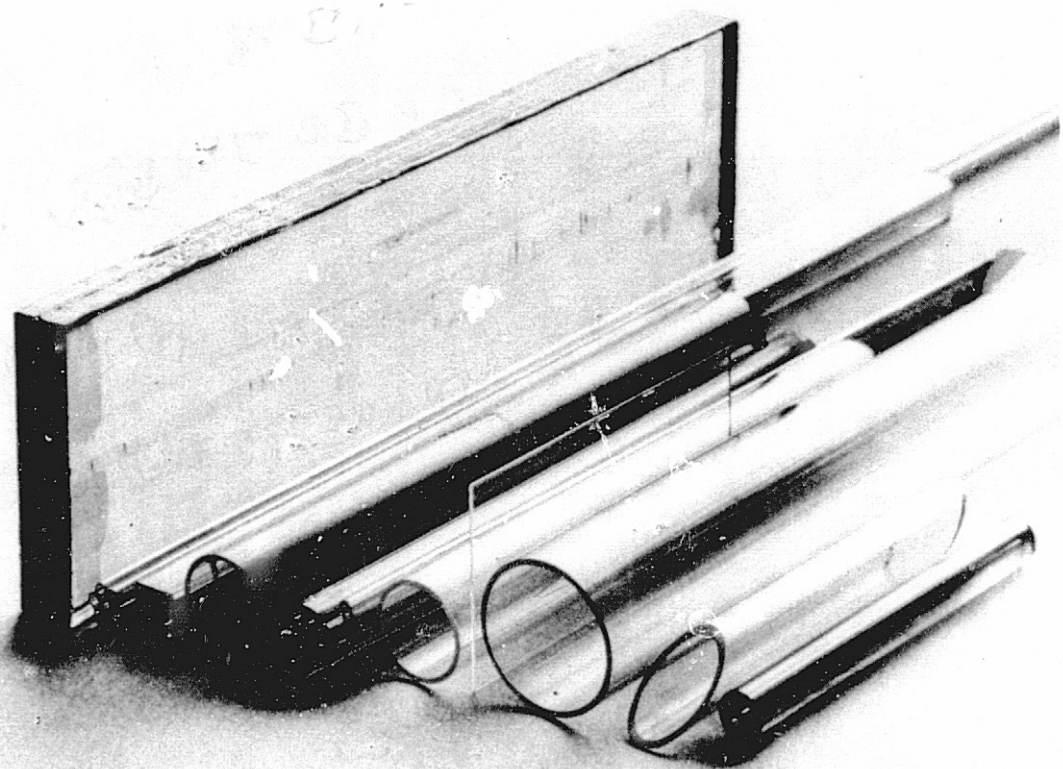


Fig. 3. Sapphire Shapes

- DIE MATERIALS, CONFIGURATIONS
- CRUCIBLE
- FURNACE DESIGN
- DETAILED UNDERSTANDING OF GROWTH MECHANICS:
  - INTERFACE SHAPE REQUIREMENTS FOR SINGLE CRYSTAL GROWTH
  - STABILITY OF STEADY STATE GROWTH CONDITIONS
  - COMPOSITION CONTROL (DOPING)

Fig. 4. EFG Applied to Silicon Ribbon -- Problem Areas



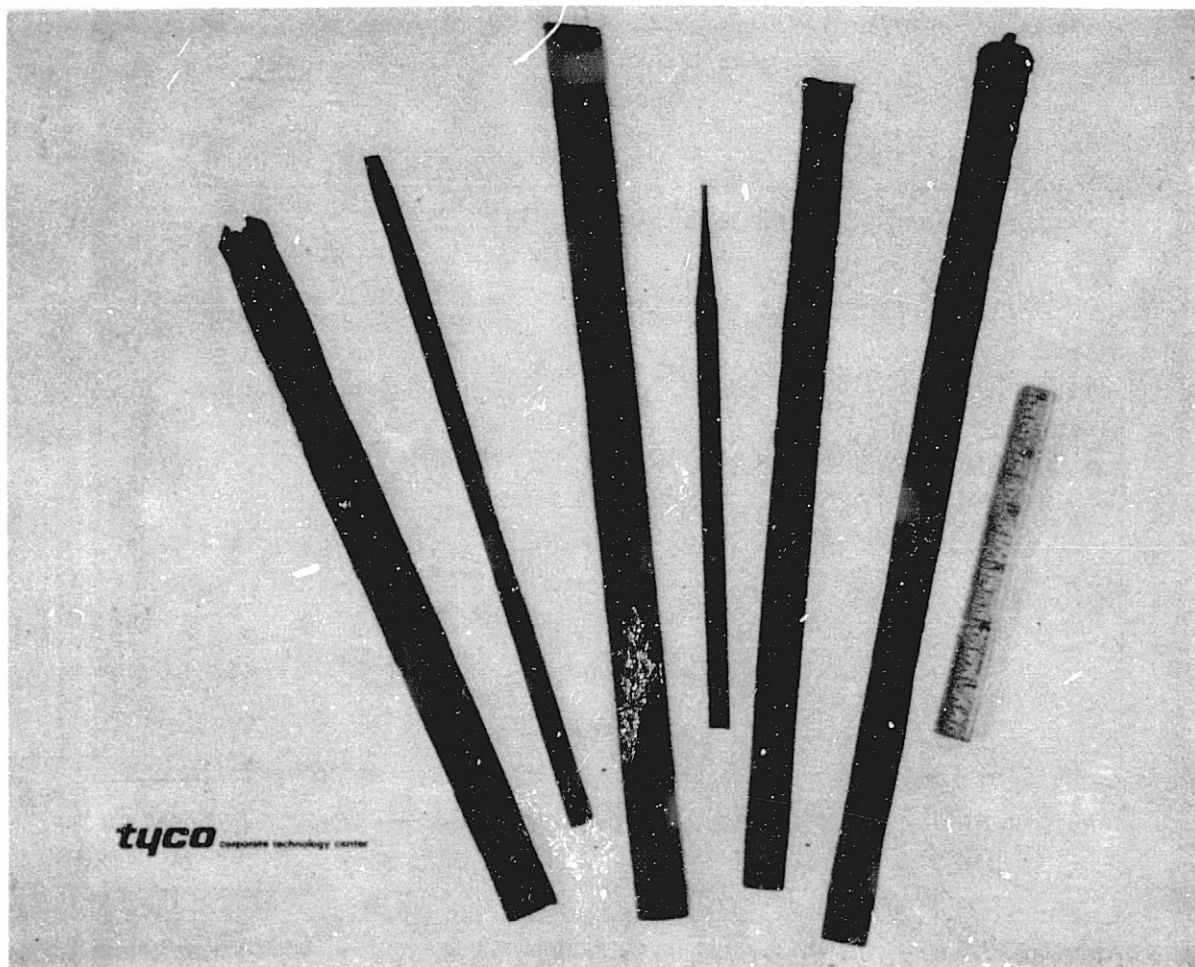


Fig. 5. EFG Silicon Ribbons

**DIMENSIONS:**      **LENGTH:** TO 15 IN.  
                         **WIDTH:** TO 1 IN.  
                         **THICKNESS:** (DOWN) TO 0.012 IN.

**RESISTIVITY:**      (UNDOPED) 1 - 10 OHM-CM P-TYPE

**HOLE MOBILITY:** 300 CM<sup>2</sup>/V-SEC FOR 1 OHM-CM

**CRYSTALLINITY:** SOME COMPLETE SINGLE CRYSTALS;  
                         TYPICALLY CONTAIN LOW ANGLE  
                         GRAIN BOUNDARIES

Fig. 6. Properties of EFG Silicon Ribbons

**PHASE I:** ONE RIBBON, 1 IN.  $\times$  0.008 IN. CONTINUOUS, WITHOUT MELT REPLENISHMENT

"UNIT OPERATION" CONSISTING OF 8 MACHINES

RAW SILICON COST OF \$30/LB

SILICON USEAGE EFFICIENCY TO RIBBON: 80%

YIELD OF GOOD RIBBON FROM RIBBON PRODUCED: 70%

ANNUAL OUTPUT: 3,024,000 IN.<sup>2</sup>

MANUFACTURING COST:\* \$409,500

RIBBON COST: 13.5¢/ IN.<sup>2</sup>

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**PHASE II:** 20 RIBBONS CONTINUOUSLY, 2 IN.  $\times$  0.004 IN.

"UNIT OPERATION" CONSISTING OF 12 MACHINES

RAW SILICON COST OF \$10/LB

SILICON USEAGE EFFICIENCY TO RIBBON: 90%

YIELD OF GOOD RIBBON FROM RIBBON PRODUCED: 70%

ANNUAL OUTPUT: 290,304,000 IN.<sup>2</sup>, 97,500 LB

MANUFACTURING COST:\* \$2,291,420

RIBBON COST: 0.79¢/IN.<sup>2</sup> OR \$23.5/LB

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\*LABOR AND MATERIALS AND MANUFACTURING O/H, INCLUDING ALL UTILITIES AND EQUIPMENT DEPRECIATION.

Fig. 7. Economics of EFG Silicon Ribbon

## SOME COMMENTS ON RIBBON GROWTH OF SILICON

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### Presentation Summary

Today's silicon crystal growth technology is one of the best-developed technologies in the field. Silicon crystals of highest perfection can easily be mass-produced, and crystals several feet long and approximately 3 inches thick can be grown using the Czochralski or float zone technique. Recently (Ref. 1), it was pointed out that standard silicon growth techniques are not efficient enough to supply the large amounts of silicon that will be needed if silicon solar cells come into play as a means of providing cheap solar energy for terrestrial applications. The need of growing long single-crystal ribbons through an economical process was also mentioned in this context. Ribbon growth has always enticed the imagination of the semiconductor materials scientist because it would eliminate sawing and polishing of silicon crystals (Ref. 2). Recent findings about the influence of residual mechanical damage (microsplits) in silicon surfaces on carrier lifetime have given more emphasis to this desire.

As a result of previous work there are two techniques available to grow silicon crystals in ribbons. These techniques are known as the web dendrite (Ref. 2) and the EFG (Ref. 4) technique.

The web dendrite growth of silicon was explored in the 1960's and is quite well understood. Silicon web dendrite crystals approximately one inch wide and of reasonable perfection and also of device grade quality were produced at the time but were not competitive with Czochralski crystals.

The feasibility of silicon ribbon growth using EFG was first successfully demonstrated by T. Cizek (Ref. 5) using a carbon die and recently confirmed by H. E. Bates, et al. (Ref. 6). Although both groups reported the growth of single-crystal silicon of high perfection, the mass production of silicon ribbon using EFG is not yet possible. The carbon die, so far the only material found useful for silicon EFG, deteriorates fairly rapidly. Consequently, EFG silicon is normally of lower perfection than desirable and continuous crystal growing of silicon as envisioned (Ref. 4) is not yet possible.

Comparing the potential of web dendrite and EFG growth of silicon, we favor EFG as a means of providing low-cost silicon. However, we clearly recognize that EFG is a high-risk program and far from supplying useful silicon. EFG requires substantial resources to make it go.

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**Discussion**

- Q: Have you tried measuring lifetime by the MOS technique?
- A: We have not advanced to that level yet, because the crystals produced at our lab were not good enough to consider it worthwhile to start device work.
- Q: How deep was the surface damage on the EFG?
- A: It goes down to about 50 microns.
- Q: How far down is damage from the sawing?
- A: In the Czochralski crystal the damage can vary, depending on how you measure it and how you slice the crystals. However, to give you an average number, damage after slicing, using the standard ID technique, can extend down to 100 microns. The damage distribution normally is much more. You will observe a very uniform damage and a non-uniform damage. The uniform damage is around 50 microns while the non-uniform damage can go down considerably deeper. I have seen it down to 150 microns. As you know, the residual damage is the way to prove the non-uniform damage. Chemical etching will not remove the non-uniform damage completely; the little split in the lattice is very difficult to remove.
- Q: How would you insure that the damage you have observed in these beveled samples was not the result of the preparation of the samples?
- A: First of all, the cracks are the result of beveling. We use that technique to reveal strain which is present in the surface. If there is no strain present in the surface, it would not crack the material.
- Q: Based on your earlier results, are you saying that all points of the EFG silicon are comparable to a slice of Czochralski silicon as relative to devices?
- A: Not today. I think that EFG poses some ferocious problems which are a great challenge to everybody in the materials field, and I think they could be overcome. Obviously, the toughest problem is the die problem. Once we have this under control, the rest should be fairly simple. Everything is geared to the die problem; whoever solves the die problem has something really going.
- Q: The apparent assumption is that these defects and damages are affecting the solar cell performance immediately. What kind of defects on surface deposits will actually affect the solar cells' performance?
- A: You are talking about solar cells and I am not really a specialist on solar cells, but I understand the influence of defects on lifetime in silicon and there is a direct correlation.
- Q: There is much difference between the crystal lifetime and the lifetime of optimum devices. Normally, a very good crystal has a millisecond lifetime. After making a p/n junction by diffusion, the lifetime drops to 10 microseconds, so I think this is a heat-dependent process. Do you agree?
- A: Yes. All these things are process dependent. We learn to control the process in such a way that we don't foul up the lifetime. That's challenge number one today in silicon technology. If you want to make a computer on something like this, you had better learn it or forget about it. I agree with your statement but I don't say that we have reached the optimum yet. There are many things we have got, and can improve, in silicon technology. To top this we must learn to control lifetime by the process in silicon. I think there will be the big payoff even for solar cells and we have not reached the optimum yet. I am talking only about single-crystal silicon; polycrystalline silicon is a different situation. We don't talk about lifetime in poly now.

## VIOLET CELL REVIEW

R. M. Fiandt  
Centralab, Globe Union, Inc.  
El Monte, California 91734

### Presentation Summary

The violet cell, so named by Comsat, provides a significant increase in output due to an enhanced sensitivity to the violet and ultraviolet section of the solar spectrum. It is a silicon solar cell having the electrical and physical attributes normally associated with silicon solar cells.

We at Centralab feel that the Comsat team of Dr. Joseph Lindmayer and James Allison, under the direction of Dr. Edmund Rittner, have made a significant contribution to users of solar energy conversion both in space and also for potential terrestrial systems where it is equally applicable.

The percentage output increase can be defined as anything from 20 percent to 35 percent, dependent upon the basis of comparison, the resistivity of the silicon crystal, the method of measurement of output per unit area, the type of coverglass, if any, and the percentage of yield to the rather normal production distribution curve.

Cutting through all of this, it is anticipated that an overall economical specification for space will provide for a cerium glassed cell output average in the 70-mW range with cell values ranging from perhaps 66 mW to 74 mW. Terrestrial systems can expect equivalent increases in output.

The violet cells involve techniques to significantly reduce the upper cell layer, thereby increasing the ability to convert and collect the violet and ultraviolet wave lengths. This necessitates an improved system for collection of the electricity generated across this more highly active and resistive surface.

The total package also involves a new tantalum oxide antireflective coating that is transparent over this wider spectrum range. This coating also has a high index of refraction to match the adhesive. Other improvements include metal contacts which eliminate titanium and a solderless metal system compatible for either soldering or welding. (Both front and back will have a silver surface.)

These proprietary improvements permit proportional increases in the design capacity of either a given spacecraft or terrestrial application. From another viewpoint, a longer useful life can also be expected when starting from a higher solar efficiency. Radiation test data indicates an actual improvement over 1-3 ohm-cm conventional cells, thereby again indicating increased life in space use. Violet cells are soon to be flown on NASA SPHINX and IMP-J satellites.

When space cells and data are available, we fully expect to provide a comprehensive standardized electrical and physical specification. This standard specification will provide all the parameters required by the design engineers and will constitute a guarantee of the same. For instance, these standardized cells will have a guaranteed average output in mW, and a guaranteed minimum mW output. Also specified will be the size, weight, metallization for either soldering or welding, and ability to pass standard qualification life and cycle tests. Certified test data will be available.

We at Centralab Semiconductor believe such a standardized product is greatly needed in this industry. In addition to simplification of designing, such standardized cells will result in a significant cost savings during manufacturing, which will benefit the industry in general. We even believe it is not impossible to envision industry acceptance of cells from stock that have been specifically inspected, tested, and approved by DCAS (Government Source Inspector) on an identifiable lot basis; again, at a cost and price savings to the industry.

For terrestrial applications, we are confident that the increased efficiency is especially applicable to potential poly- or single-crystal systems. We feel it is particularly useful for concentrator systems due to the highly efficient current collection system which minimizes IR losses across the surface. It is also notable that any terrestrial system cost increase for the violet cell efficiency will be insignificant.

Presently, we are optimizing the various manufacturing procedures in order to lock in on the most advantageous process specification when considering functions, reliability, and cost. We are producing between 50 and 100 space cells daily and expect to complete this phase before the end of the year. Therefore, the final standardized specifications, prices, and cell production capability will be available about January 1974.

### Discussion

- Q: I feel just a little bit disheartened by the fact that you said that 70 milliwatts is 12.5 percent. At least 204 cells had a 13.5 percent efficiency range for our cells.
- A: I think this illustrates the point of confusion that I mentioned before because I think that when we are talking about manufacturing commercially, we are trying to use, say 75 or 80 percent of the distribution of the cells that are made and Dr. Lindmayer is talking about some 20 or 25 percent and, you see, this is where you get into problems. There are cells like that, but they cost a lot more than the 75 or 80 percent cells.
- Q: Can you say how you handle the higher surface resistivity of the violet cell design; is it finer gridding or do you use some other techniques?
- A: It's a very fine gridding from 40 to 60 lines per inch, but maintaining the surface area comparable to the very narrow lines.
- Q: Can you say why you want to eliminate titanium?
- A: Well, there is an interesting thing, and I am not the scientist, I only run the plant, but it has to do with moisture. There has been a persistent feeling throughout the industry, and I don't know that it is completely justified, but for some applications there has been some feeling that titanium allowed moisture damage.
- C: I might add, too, that titanium proves itself to be rather harmful if you have any imperfection present when you diffuse the junction. You are much more apt to get shunting, which then lowers the fill factor somewhat.
- A: It certainly has to be highly controlled.
- C: I would like to make a comment for Heliotek. We have produced cells, although we did not benefit from paying the five percent royalty for the Comsat license, with 180 milliamperes short circuit current, and we believe that this can be improved upon. We also feel that the production of solar cells on which we are doing pilot lots right now will run significantly higher than 70 milliwatts average, and I believe that we would tend to agree with Dr. Lindmayer that there is even more that is possible there, as opposed to the situation a year ago. At Heliotek we are very encouraged by what we see in working on these higher efficiency cells and by paying attention to the recipe that we are using in making solar cells out of the raw silicon that we buy and pay for. I think that we are going to find that we are in a transient period now where the average cells that will be produced a year from now may be considerably higher than 70 milliwatts output for a two by two.
- A: Thank you. I completely agree with that. We expect the same thing.
- Q: The job standards on your production are 50 - 100 cells daily?
- A: No, this is just a prototype sort of thing. This is just work we are doing to standardize our processes and to optimize them. It has nothing to do with the many thousands a day that . . .
- Q: I understand, but it is 50 to 100 cells?
- A: Yes.

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## FUTURE COMSAT SOLAR CELL DEVELOPMENT PLANS

E. S. Rittner  
COMSAT Laboratories  
Clarksburg, Maryland 20734

### Presentation Summary

Following the transfer of technology to Centralab for fabricating the COMSAT Violet Cell, it is planned to attempt improvements in the space-qualified silicon cell in the following areas:

- (1) Reduction in overall reflectance (since a single anti-reflection coating suppresses reflection completely at only one wavelength),
- (2) Reduction of minor recombination losses at the back contact,
- (3) Improvement in radiation hardness which would then permit still further improvement in beginning of life efficiency.

With respect to terrestrial solar cells based upon single-crystal silicon, it should be noted that the cells of highest performance presently available have been optimized for use in space under a hostile radiation environment. The trade-offs for best cell performance at sea level will be significantly different. It is highly recommended that the efficiency of the silicon cell be optimized for terrestrial use well before fabrication processes employing automated machinery to effect drastic cost reductions are frozen.

### Discussion

(See "Violet Cell Review," by R. M. Fiandt in this session.)

## STATUS OF SILICON WEB SOLAR CELLS

R. K. Riel  
Westinghouse Research Laboratories  
Pittsburgh, Pennsylvania 15235

### Presentation Summary

Silicon solar cells are ordinarily prepared from cylindrical single crystals grown by either Czochralski or float-zone processes. Diffusion blanks are formed into rectangular shapes by sawing, lapping, polishing, and etching.

Silicon has also been produced in ribbon form of proper dimension directly from the melt. Lapping, polishing, and etching are not required and the material is ready for device processing. This silicon web process was developed by Westinghouse. The ribbon is grown in the [211] direction yielding (111) web surfaces.

A web solar cell program was initiated in 1960 and by 1966 to 1967 Westinghouse had installed a pilot line at its Semiconductor Division. The last product from this line was a radiation-resistant drift-field solar cell 30 cm long and 1 cm wide. Production capability was approximately 1000 cells per month having efficiencies under AMO conditions of 9 to 12 percent and 10 to 14 percent under AM1. Both p on n-type and n on p-type cells were also produced on this line in large quantities with efficiencies equivalent to other suppliers using conventional materials.

Silicon web drift field cells were flown during 1966 to 1967 in various satellite experiments and demonstrated satisfactory results. Hughes Aircraft and Westinghouse, under contract to the Air Force Aero-Propulsion Laboratory in 1966 to 1967 produced a large number of cells for investigations in flexible arrays. These 30 cm X 1 cm cells were assembled into a 100-watt array and passed environmental conditions required for launch. Westinghouse also investigated new techniques for panel assembly.

Terrestrial application of photovoltaic conversion for power generation requires a sizeable cost reduction. In our opinion, one option as a first step is to investigate cost reduction in silicon web. The silicon web growth program at Westinghouse which started in the 1960's provided crystals that could be grown regularly with some degree of reproducibility. Silicon web with a usable width of 1 cm was produced on a pilot line, and wider web (3 cm) was produced in the laboratory. As the width of the material increased, however, so did problems with dislocations generated in the bounding dendrites. Unless the thermal conditions were exactly correct, the dislocation density rapidly increased to the point where the web became polycrystalline. With appropriate thermal conditions, however, wide thin web (3 cm wide) could be grown in lengths up to 4 feet.

Although the growth of wide web was a significant achievement, an even more important result was the identification of two major problems blocking the road to further development of this process:

1. The development of a quasi-continuous feed/grow system to permit truly steady state growth conditions.
2. The development of an appropriate crucible and heater design to permit more active control over the temperature distributions in the melt near the growing interfaces and in the web itself immediately above the melt.

Obviously, the solutions to the problems are mutually dependent since the melting of the feed material could affect the liquid temperatures in the growth region.

The specific areas of endeavor needed are (1) to analyze the thermal, mechanical, and material requirements of the web growth technique and (2) to arrive at a conceptual design for a laboratory system. This system would necessarily provide a means for quasi-continuous growth of web crystals from a thermally controlled crucible. The

investigation could also identify the means that might be used for automatic control of the growth process. A goal of 6 cm wide seems to be reasonable at this time. Labor and equipment cost reduction, through automation if possible, is of utmost importance.

Westinghouse has reviewed the NSF/NASA Plan for Low Cost Solar Array Technology Development reported in *An Assessment of Solar Energy as a National Energy Resource* (as Figure 17 on page 66), December 1972. This is a good plan for silicon development and should provide a good basis for initial efforts.

Most of the investigations on silicon web solar cells have been supported by the United States Air Force Wright-Patterson Air Force Base in the Air Force Materials Laboratory and the Aero-Propulsion Laboratory. Small array projects were supported by NASA.

## Discussion

Q: Did you make a cost projection on continuous growth technique on your previous work to get a cost per square centimeter or cost per cubic centimeter?

A: You mean a cost projection if we used this method now. No, I don't think we've made a cost projection. I think that later on Dr. Wiener, who is with our Power Systems Group, will touch on this. He will probably say that in order to get at this thing, it is probably somewhere around ten cents a watt that you are going to have to get to. I'll let him comment on that when he comes here and talks, rather than my doing it.

Q: I wonder if you or someone else could make some comments regarding a program at Ion Physics in which they use this sort of cell with their ion implantation technique?

A: What kind of comment do you want?

Q: Regarding the kinds of efficiencies, and whether it looked economically feasible.

A: Yes, Ion Physics, working with us somewhat and also working with Ced Currin's group, did prepare cells on silicon web. As I recall the efficiencies were also quite good, and I don't know what else to say other than that. They had had a successful program.

Q: I can't help commenting about all the furor that took place in the mid-sixties regarding the web dendrite work, and it seems to me the same comment applies today, in that nobody was willing to really comment on or extrapolate the cost of these things although they were being promoted as lower cost cells as compared to Czochralski silicon cells.

A: Our feeling is that we can get at a cost that would be respectable in terms of power generation; otherwise, we wouldn't try to pursue such a program in solar cells, and we are looking at the solar cell program as both one of web and cadmium sulphide, which will be commented on later. But I say again, that it is our opinion that you are going to have to get at something on the order of ten cents per watt and that's probably what we are going to have to shoot for.

Q: Do you think that's possible with web material?

A: I think it is possible.

Q: When you say ten cents a watt, is that the cell cost or the system cost?

A: It will be a cell cost. I'd like to comment on just one or two things about what the gentleman from IBM said. The reason for getting out of the web process was not related to some of the things that he was saying; it's much more complex than that. I would also like to say that we made a strong attempt to get into the solar cell hardware business and we were not able to, but here, again, that wasn't due to the costs; it was the same old p/n- and n/p-type argument that we arrived at: we had a good radiation resistant solar cell, but we couldn't sell it to anybody. So it is, you know, how do you beat that game - you can't do it. No matter how good you make a cell, if nobody's going to buy it, you're dead.

Q: Can you say how the drift-field region was produced in these cells?

A: Yes. As I said, it was done with an epitaxial-growth technique.

Q: Were you doing epitaxial-growth?

A: Yes. We were doing doping and grading with densities between  $10^{19} \text{ cm}^{-3}$  and  $10^{15} \text{ cm}^{-3}$  in the region of ten to fifty microns, and with good control.

## THE NASA-LEWIS PROGRAM ON SILICON SOLAR CELL AND ARRAY TECHNOLOGY

D. T. Bernatowicz  
NASA-Lewis Research Center  
Cleveland, Ohio 44135

### Presentation Summary

The NASA-Lewis Research Center is conducting a program on silicon solar cells and arrays with the objective of reducing their costs, for both space and terrestrial uses. The purpose of this talk is to outline those parts of our cell and array research and technology effort that are relevant to terrestrial uses. A portion of the NASA-Lewis program is specifically directed to terrestrial systems, and that will be described by A. F. Forestieri in the Systems session.

Our work consists of technology improvement and research, done both in-house and on contract. The technology effort seeks to develop higher efficiency cells, lower cost cell fabrication methods, and lower cost array fabrication methods. The present technology efforts are listed in Table I and include development of a 13½ percent (AMO) cell with wraparound contacts, development of the plastic (FEP)-covered solar cell module, and investigation of other cell fabrication methods.

The research effort seeks to raise the efficiency of silicon cells to the practical limit of 18 percent in space or 21 percent on Earth. The present efforts (Table II) include identifying and understanding the loss mechanisms in low resistivity silicon, especially those contributing to high leakage currents, and constructing an analytical model for the solar cell that includes all loss mechanisms.

### Discussion

- C: I think that one of the things that is a little bit confusing about the cost problem, and maybe the suppliers purposely make it so, is that there is a cost of material and there is a transaction cost; a \$20.00 a watt figure and a \$5.00 a watt figure that were presented that have to do with the average transactions taking place in the United States this year. Most of these systems are very small, 4 to 10 watts, maybe 20, maybe 50 watts, so there is an attendant cost for doing business in small sizes of low volume/area that adds quite a bit. So it's not all packaging and it's not all other costs besides the cell. The cells are still the main problem and the business is too small.
- C: I have one other thought in regard to the system costs. Now I don't know what the definition of a system is, but I would assume that a system will have to employ some power conditioning output. I am sure you are aware of the fact that people are working in the area of large blocks of power conditioning on large devices and trying to reduce the cost of these devices. Now, on other programs you just don't hear about it because they are associated with something else; so this is being worked out.
- Q: When you say that FEP is compatible with terrestrial applications, are you actually basing this on longevity or what?
- A: Longevity. I don't want to steal Forestieri's thunder, so he will give you so. results of what we have done and why we think it is going to work out for terrestrial too.

Table I. Solar Cell and Array Technology

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**OBJECTIVE:** Reduce the cost of solar cell arrays for space and terrestrial applications.

**APPROACH:** Develop high-efficiency cells  
Develop low-cost cell fabrication methods.  
Develop low-cost array fabrication methods.

**TASKS IN PROGRESS:**

- (1) Advanced Si cell development - CENTRALAB - \$81K
  - (2) Advanced Si cell development - HELIOTEK - \$86K
  - (3) Advanced Si cell development - IH
  - (4) Vapor deposited Si solar cells - IH
  - (5) Primitive solar cell fabrication - IH
  - (6) FEP-covered solar cell module - TRW - \$250K
  - (7) FEP module improvements - IH
- 

Table II. Solar Cell Research

---

**OBJECTIVE:** Raise the efficiency of Si solar cells to near 18% (AMO) or 21% (AMI)

**APPROACH:** Find, understand, eliminate losses.

**TASKS IN PROGRESS:**

- (1) Contributing causes of leakage current - CENTRALAB - \$58K
  - (2) Contributing causes of leakage current - IH
  - (3) Effect of diffusion profile and surface treatment - IH
  - (4) Study of surface states and surface leakage - IH
  - (5) Effect of guard ring structures on leakage current - Wayne State Univ. - \$13K
  - (6) Interpretation of measured L - IH
  - (7) Theoretical analysis of solar cells - N.C.S.U. - \$27K
  - (8) Theoretical analysis of solar cells - IH
-

## A PROPOSED SCHEME FOR THE VLS GROWTH OF SINGLE-CRYSTAL SILICON SHEETS

A. S. Blum  
Washington University  
St. Louis, Missouri 63130

### Presentation Summary

The growth of long, slender, single-crystal silicon whiskers from the vapor has been explained by R. S. Wagner, et al. (Refs. 1, 2, and 3) in terms of the presence of a layer of molten, metal-silicon alloy on the growing whisker tip. Their work demonstrated that one could deliberately produce tall, thin columns of silicon by placing a small spot of metal on the  $\{111\}$  face of a silicon wafer and heating in the presence of a silicon-bearing vapor. The preferential growth on the liquid, metal-silicon alloy-covered surface is ascribed to the larger accommodation coefficient of the liquid. Figure 1 illustrates the growth process. The cross sections of the grown columns are shaped by the tendency of the molten droplet to assume a circular form (in its circularly symmetric environment) minimizing its surface energy and by the possible orientations of the crystal planes which must compose the sides of the column. Three-, six-, and twelve-sided columns have been observed (Ref. 2).

In order to grow single-crystal sheets, some alteration of the symmetry of the liquid droplet's environment must be provided. A possible example of such would be to attempt growth on the narrow (111) edge of a silicon wafer, as shown in Fig. 2. Here one is depending upon the interfacial energy to draw the molten alloy into an elongated shape covering the edge of the wafers. In Fig. 3 a proposed assembly of such sheets, growing in a furnace supplied with  $\text{SiCl}_4$  and  $\text{H}_2$ , is illustrated. The sheets are withdrawn from the furnaces as they grow. This process is continued until the metal is exhausted by solidification into the growing crystal or by reaction with the Cl ions liberated during the growth process.

A second arrangement which would further reduce the surface tensional energy while increasing the interfacial energy is illustrated in Fig. 4. In this case, two edges of two separate sheets support the elongated molten zone by capillary action. Using the apparatus sketched in Fig. 5, the molten zone is surrounded by a  $\text{SiCl}_4$ ,  $\text{H}_2$  mixture. The sketch shows two units of a presumably much larger assembly of such units, all having a common heating apparatus. As growth occurs, the two sheets are slowly moved to maintain a constant-width molten zone.

The apparatus sketched in Fig. 5 is heated by the indicated induction coil. This heating source offers several advantages over simply placing the silicon in a resistance-heated furnace at uniform temperature. The peak temperature and source of heat occur near the growing edge, discouraging droplet migration away from this edge (Ref. 3). Growth on those faces of the sheet which are not covered with the molten alloy is slowed because of their cooler temperature. If a suitable metal atom bearing gas could be identified, the metal in the alloy could be continually replenished. Finally, if the magnetic field is arranged to be normal to the silicon sheets, an excessive pull rate should widen the molten zone, increasing the absorbed power and temperature. The growth rate should increase as a consequence. This property should simplify the problem of controlling the pull rate.

Based upon existing work with platinum, growth rates between 0.6 inch and 1.0 inch per 24-hour period should be possible (Ref. 2). In an effort to increase the rate of area grown per enclosure and per heating apparatus, it may be possible to include several pairs of growing sheets in one of the indicated enclosures. The use of metals other than platinum may enhance the growth rate. A stack of identical units (two of which are shown in Fig. 5) can share a common induction heating source.

## References

1. R. S. Wagner, W. C. Ellis, K. A. Jackson, and S. M. Arnold, "Study of the Filamentary Growth of Silicon Crystals from the Vapor," *JAP*, Vol. 35, No. 10, October, 1964, pp. 2993-3000.
2. R. S. Wagner and W. C. Ellis, "The Vapor-Liquid-Solid Mechanism of Crystal Growth and Its Application to Silicon," *Trans. Met. Soc. AIME*, Vol. 233, June, 1965, pp. 1053-1064.
3. R. S. Wagner and C. J. Doherty, "Controlled Vapor-Liquid-Solid Growth of Silicon Crystals," *J. Electrochem. Soc.*, December, 1966, pp. 1300-1305.

## Discussion

Q: What temperature is the melt?

A: These have been grown over a fair temperature range, but it is about 1000°C.

Q: You mentioned three metals, all of which give lifetime trouble. Can you comment on whether you can get rid of gold?

A: Yes. I think some interesting experiments have been done in this area. The growth of an oxide layer on the surface of the silicon material is a common processing step and by combining that with a low flow of hydrochloric acid, there have been some dramatic increases in lifetime as reported in the Electrochemical Society. Of course, the work hasn't been done yet, so one can only speculate about it, but it is possible that one could have a really dramatic increase in restoration of the lifetime. In fact, in thinking of a process where you are going to do this economically, you might have to try to recover that lifetime.

Q: Don't your metals disappear as they freeze?

A: Yes, they do.

Q: How well can you control the thickness by the thermal gradient?

A: Let me make a comment on the disappearance first. They disappear by inclusion into the solid as it grows and by reaction mainly with the hydrochloric acid that would form. So the process would terminate after a period of time if you didn't restore the metal, and one of the things that one might hope for is that by induction heating and having a molten zone, you could possibly get a metal-bearing gas that would restore the metal. Now, other than that, I think you would be limited. If you can't do that, you might be limited to a growth of, say, 20 inches or so.

Q: How well is the thickness controlled?

A: You can see some of the columns there. All I can say really is that they look quite straight. That was heated in an oven isothermally and did not have just a small region being heated and grown there. The columns look very straight; I am limiting myself to the ones that have been grown. I am not sure what would happen in an induction heating system.

Q: Wouldn't there be a natural tendency to develop octahedrals?

A: No, in the columns in sheet growth, the crystal planes are the same ones as were present in the columns.

Q: There are surface tensions on the droplet and you want to maintain an elongated droplet. However, the heat tends to reduce the surface tension.

A: Right, there are steps that would develop. The thing would narrow by developing steps on the side, possibly where there are preferential growth sites, so I don't know. The columns look quite straight.



**Q:** If your metal actually disappears into the crystal, does our deep trap impurity get removed?

**A:** I think that was the same question that Mr. Rappaport raised and was what I suggested that you might have to do. For instance, silicon has been doped with gold, shortening the lifetime dramatically, and then heated in an oxygen atmosphere, dry oxidation with a trace of hydrochloric acid; the lifetime recovers have been pretty much back to the original -- quite large, many microseconds.

**C:** The growth rate is much too large from our experience with solution growths. If you lower it to something like four millimeters a day, I think this inclusion would disappear.

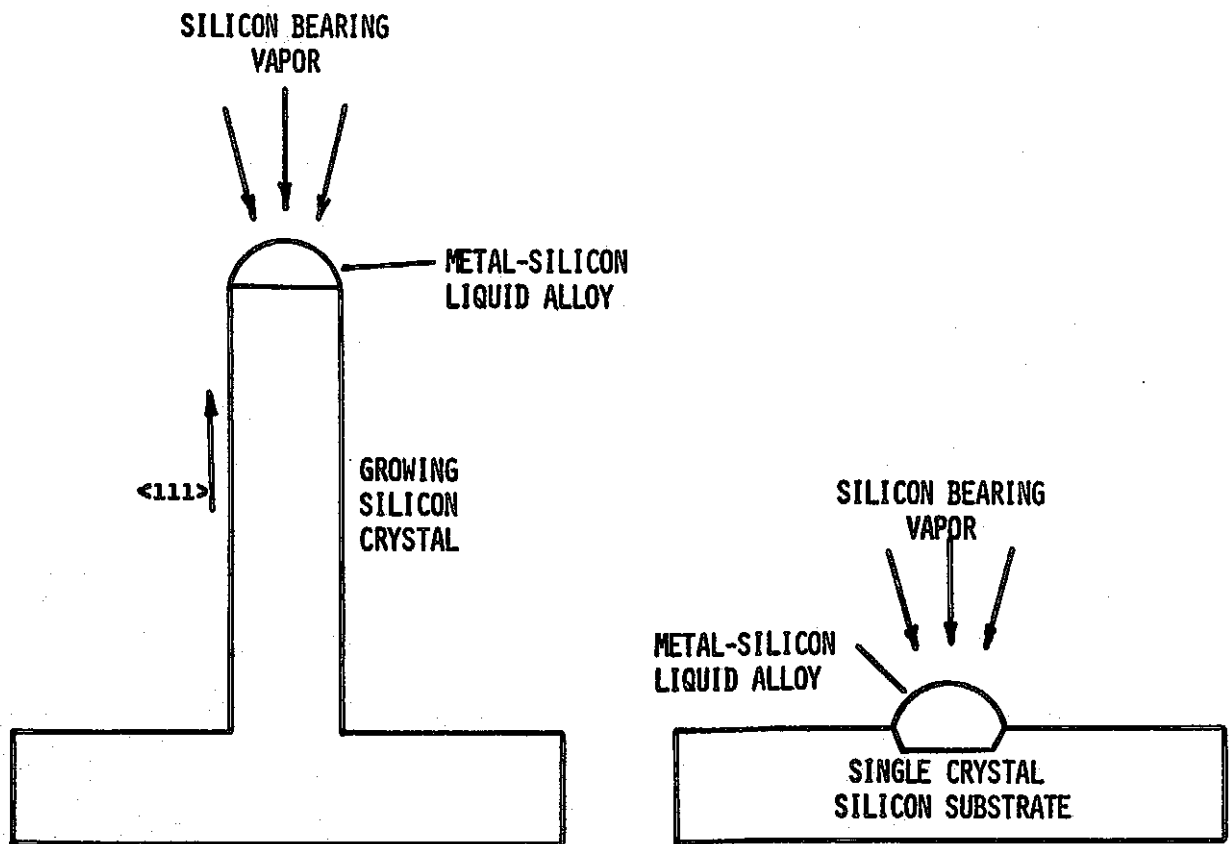


Fig. 1. A Figurative Illustration of the VLS Growth Process (Ref. 2)

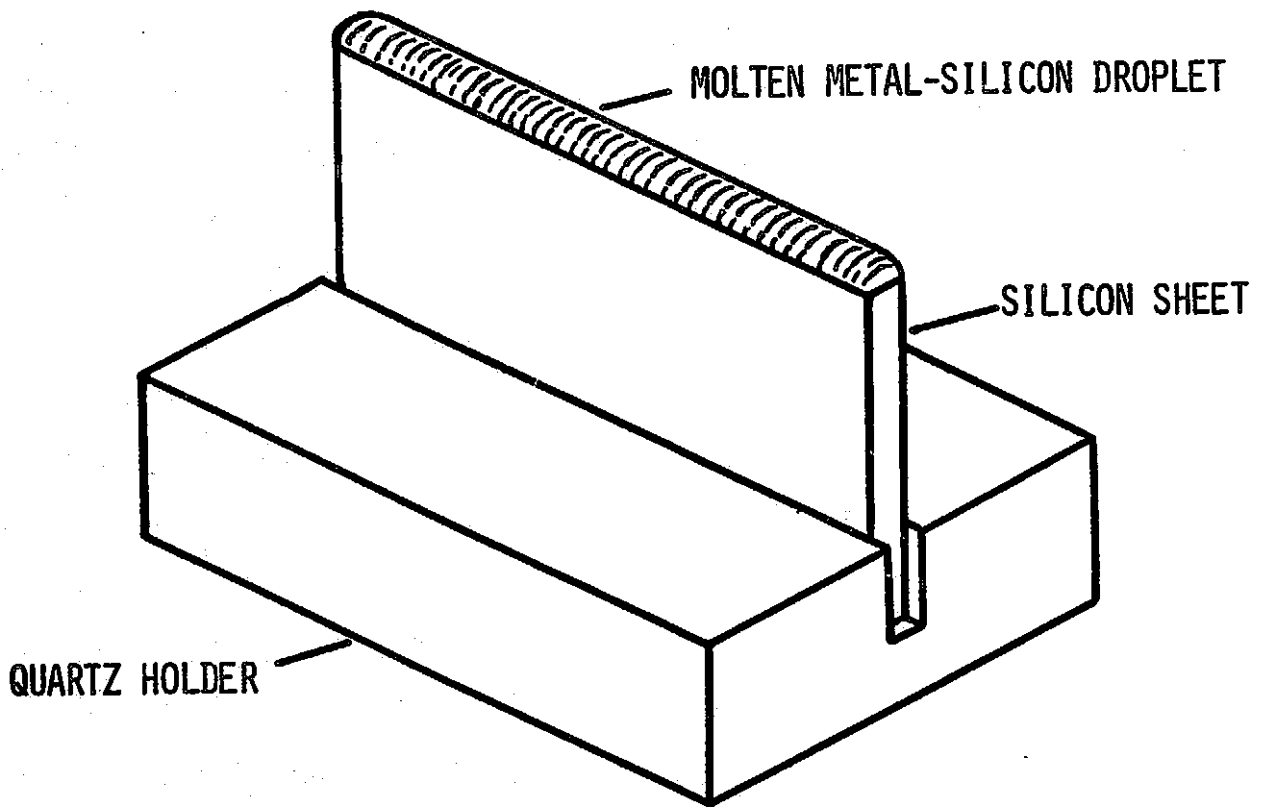


Fig. 2. An Elongated, Molten, Metal-Silicon Droplet Supported on the Edge of a Silicon Wafer

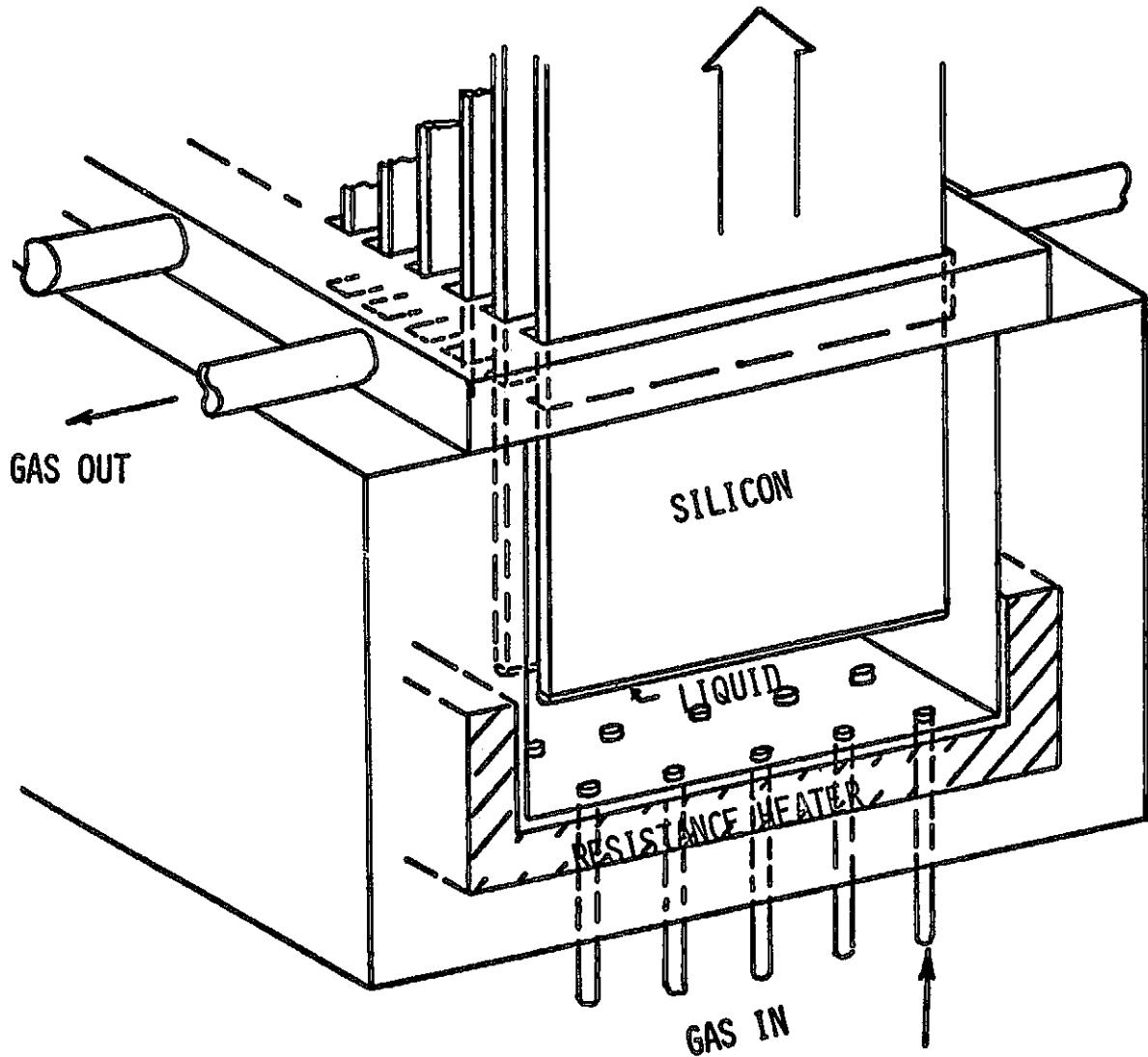


Fig. 3. A Resistance-Heated Furnace for VLS Growth of Single-Crystal Silicon Sheets

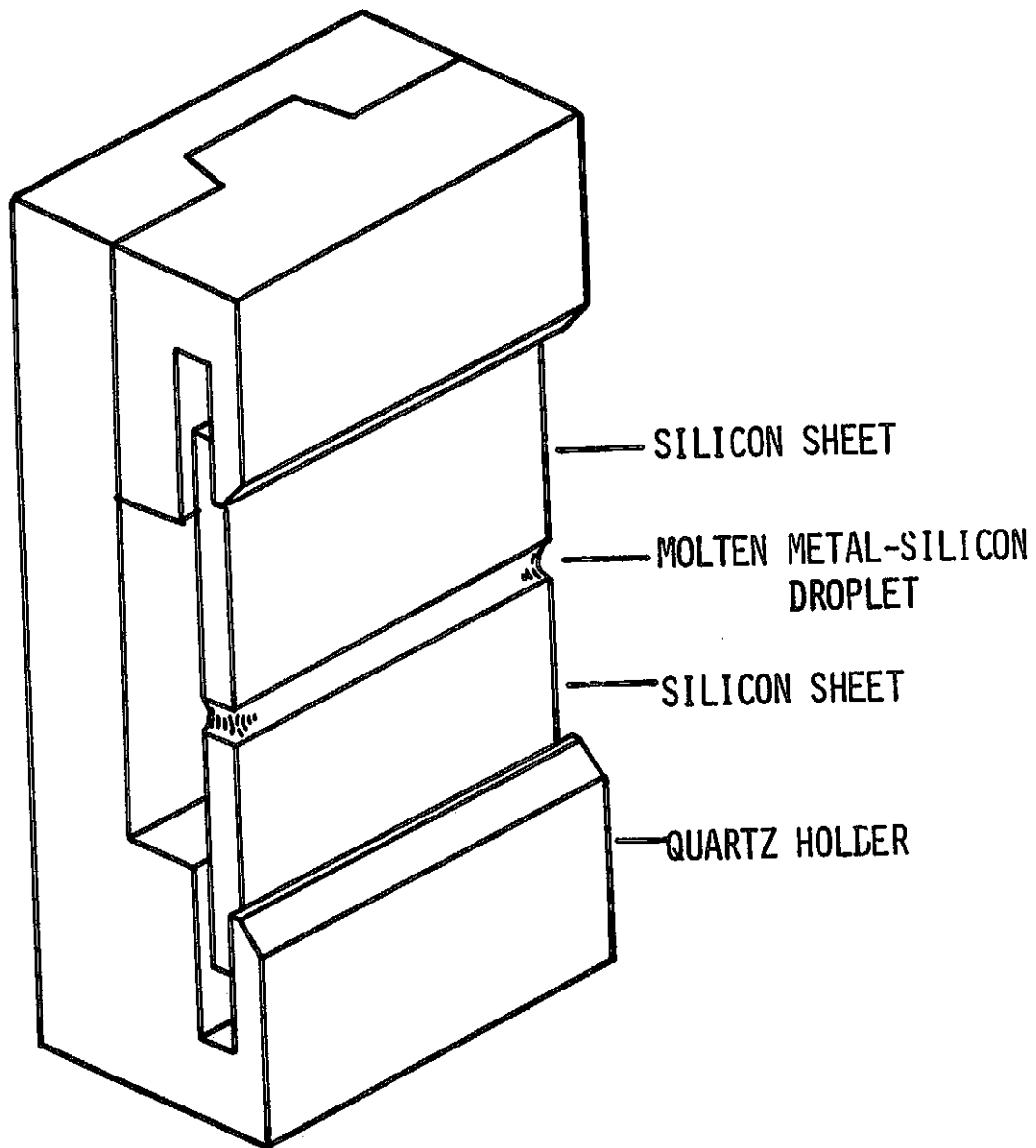


Fig. 4. A Molten, Metal-Silicon Droplet Supported, by Capillary Action, Between the Edges of Two Silicon Sheets

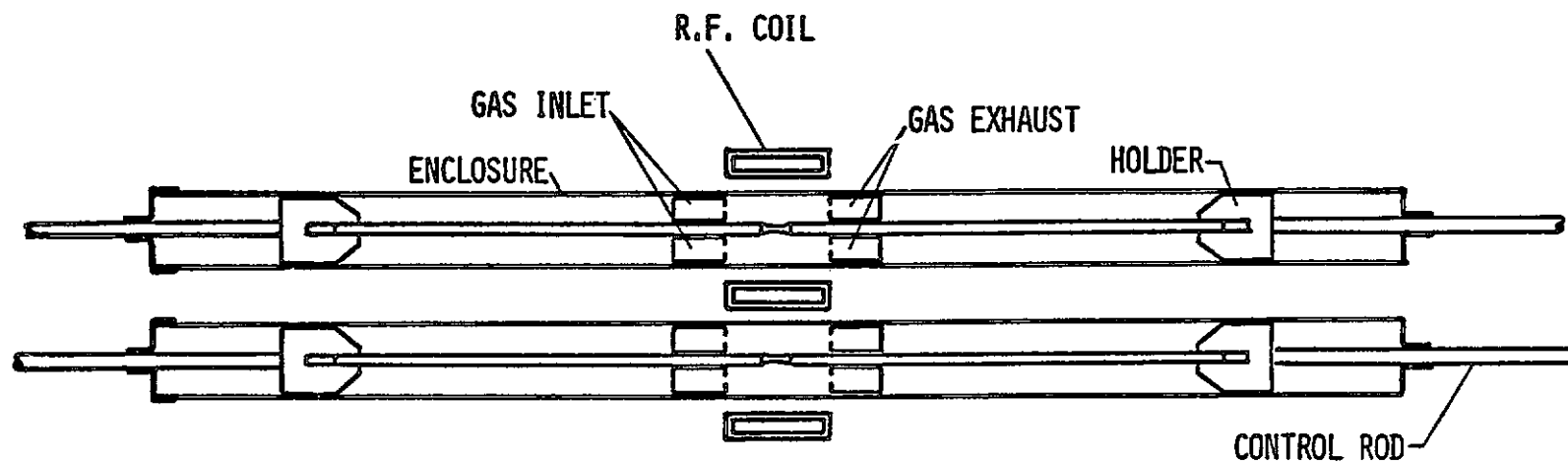


Fig. 5. Two Units for Enclosing, Supplying Gas, Supporting and Positioning Silicon Sheets for VLS Growth. The Liquid Region Is at the Center and Is Supported, by Capillary Action, Between the Growing Ends of the Sheets. The Units Are Induction-Heated

**SESSION II**  
**POLYCRYSTALLINE SILICON**

## **SESSION II. POLYCRYSTALLINE SILICON**

**RESEARCH ON LOW-COST SILICON SOLAR CELLS FOR LARGE POWER SYSTEMS—P. H. Fang**

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## RESEARCH ON LOW-COST SILICON SOLAR CELLS FOR LARGE POWER SYSTEMS

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### Presentation Summary

In this paper, we wish to describe the basic idea and the progress made on the research to develop a low-cost silicon (Si) solar cell design which would inherently meet the practical requirement of large power systems. The fundamental difference between our Si cells and the ordinary Si cells, such as those commonly used in spacecraft, is that while single-crystal Si slabs are used in ordinary cells, we propose to use polycrystalline Si sheets. This paper is intended to be a summary of our complete reports from which detailed information can be obtained. For convenience, we list these references below:

- A1 *Proc. Ground Application of Photovoltaic Power Sources*, Boston College, Nov. 1970.
- A2 *Fourth Proc. Ground Application of Photovoltaic Power Sources*, Boston College, April 1971.
- B1 *Low-Cost Silicon Solar Cells for Large Power Systems*, NSF Grant GI-34975, First Quarterly Report, Sept. 1972.
- B2 Ibid. NSF/RANN/SE/GI-34975/PR/72/4.
- B3 Ibid. NSF/RANN/SE/GI-34975/PR/73/1.
- B4 Ibid. NSF/RANN/SE/GI-34975/PR/73/2.
- C1 *Structure and Modification of Grains in Polycrystalline Silicon for Low-Cost Solar Cells* (Joint proposal to NSF from Boston College and Northeastern University).
- C2 *Development of a Sputtering Process to Form a p-n Junction Applicable to Low-Cost Silicon Solar Cells* (Joint proposal to NSF from Boston College and Ion Physics Corporation).
- C3 *Research on Steel as an Economical Solar Cell Component* (Proposal from Army Materials and Mechanics Research Center).

From our point of view, the essential procedures for making ordinary solar cells are:

- (I) Growth of single-crystal Si with proper doping impurity.
- (II) Slicing the crystal into thin rectangular slabs.
- (III) Formation of the p-n junction by counterdoping on one side of the surface.
- (IV) Completion of electrode connections.

The following discussions are based on these categories of procedures.

(I) Our first investigation concerns the economical aspect. Based on the most optimistic calculations, solar cells produced according to these procedures do not seem to be practical for the large scale application (A1). Therefore, we proposed to replace the single-crystal slabs of a fraction of a mm thick by polycrystalline sheets of the order of  $10 \mu$  in thickness (A2).

We note that the growth of single-crystal Si was already a well-developed topic, contributed to by numerous established laboratories for a decade before the ordinary solar cells were made. On the other hand, Si sheets, of a typical dimension of a few  $\text{cm}^2$ , have only been grown by epitaxial techniques on single-crystal Si, or, infrequently, on expensive metallic or sapphire substrates. The substrate here acts as a mechanical support and, in addition, as a nucleus for growth.

For our purpose of producing Si sheets, the criteria for success will be:

- (1) An economically acceptable and conveniently available material substrate.
- (2) The capability of growing a continuous, stable Si sheet on the substrate.
- (3) Crystalline rather than amorphous Si.
- (4) The grains of crystalline Si should exceed some minimum value.

We found experimentally that the ordinary steel, aluminum or copper all satisfy (1). By electron beam evaporation or chemical vapor deposition (we have also experimented with the sputtering technique but discontinued later because of the impractically slow rate of growth. See, however, (III) of this work), we have succeeded in growing Si sheets described in (2). To meet (3), with a vacuum of  $5 \times 10^{-6}$  torr, with a substrate temperature of 525°C or above, and with a deposition rate of the order of 1  $\mu$ /min, crystalline Si is obtained. Furthermore, we observed that these polycrystals have a preferential orientation, namely, the (220) plane of the crystal is parallel to the substrate plane. This interesting find, which has an important benefit for the fabrication of the solar cell, is discussed in B4.

For criterion (4), our work is in progress. Basically, Si morphology in most cases bears a similarity to the texture of the substrate (B2). However, a direct identification or characterization has still to be worked out (C1).

An important procedure in (1) is the impurity doping. This procedure is taken care of in the growth process of single crystals and is also quite simple in the chemical vapor deposition process (B3). In the case of electron beam evaporation, if one uses a source of Si which already contains the doping impurity, the difference in vapor pressures between Si and the doping impurity at high temperatures makes it difficult to maintain a Si source with a constant impurity concentration. We have also experimented with coevaporation of aluminum (Al) as a p-type impurity. Aluminum is evaporated from a tungsten boat heated by ac current. Because a very low relative concentration of Al is required, typically the ratio of Al/Si is to be less than  $10^{-6}$ , there is a control problem (B3). At the present, other means of doping the impurities are being investigated.

(III) Ordinary p-n junction formation is by thermal diffusion of doping gases. Ion implantation has also been reported before. One of the differences in these two processes is the temperature requirement. Normal diffusion temperatures are in the region of 1000°C while in ion implantation the highest temperature is for the annealing of the thermal damage which can be achieved by temperatures of 400 to 600°C. However, in both processes, there is an involvement of the penetration of doping ions into the Si host lattice. In this process, since the diffusion along the grain boundary is generally higher than the diffusion in the crystal (Ref. 1), a detrimental effect of the shorting of the p-n junction would result. Elaborate processes to overcome this difficulty have been reported before (Ref. 2) and other methods have been discussed in our report B3. More recently, we are initiating a program in cooperation with Ion Physics Corporation (C2) to use sputtering to form p-n junctions. The basic idea is to form a new Si layer on our Si sheet, as in the epitaxial growth, with an opposite type of impurity. In this case, there is no interatomic diffusion between these two layers of Si deeper than a few lattice constants. Therefore, there is no severe grain boundary diffusion.

Sputtering is a slow process for growing Si film. However, for the p-n junction formation, the thickness will be less than 0.5  $\mu$ . The time required in this case will be less than half an hour, which is an acceptable rate.

(IV) The two kinds of electrodes for solar cells, that of top and of bottom, will be discussed separately. For the bottom electrode, starting on the substrate, we first evaporate a layer of titanium (Ti) about 1  $\mu$  thick, or silicon oxide layer about 1  $\mu$  thick before the Ti layer. This Ti layer performs three functions:

- (1) Prevents diffusion of materials from the substrate to Si.
- (2) Acts as a nucleation center or as a center of morphological growth.
- (3) Forms an ohmic contact with Si.

All the results we have accumulated so far indicate that the Ti layer performs well functions (2) and (3). From x-ray data the Ti layer is also effective for (1). However, a more stringent test will have to wait for semiconductor measurements, such as lifetime, where a trace of diffusion from the substrate could become important.

For the top electrode, the important problem is the grain size. A general requirement will be that the grid spacing is smaller than the grain size. Here, the grains are related to the top Si layer. This differentiation is important if the top layer is formed by sputtering in which case the grain size could be different from the base Si sheet. If the grains are less than the order of mm along the surface of the sheet, a continuous electrode, such as tin oxide, instead of the common discrete grid would be used.

In conclusion, some achievements that have been made in order to fulfill the requirements of our designed Si solar cell are reported here and our continuous efforts have been indicated.

My co-workers are Prof. J. H. Chen, Linda Ephrath, Dr. T. Shaughnessy, Jack C. T. Ho, and Judy Smith.

This work is supported by the RANN program of the National Science Foundation.

### References

1. T. I. Kamins, J. Manolin, and R. N. Tucker, "Diffusion of Impurities in Polycrystalline Silicon," *J. Appl. Phys.* **43**, 83 (1972).
2. J. D. Heaps, O. N. Tuffe, and A. Nussbaum, "Vapor-Deposited Polycrystalline Silicon Solar Cells," *IRE Trans. Electronics Devices* ED-8, No. 6 (1961).

### Discussion

Q: Could you characterize the type of silicon you get by the chemical vapor deposition and how it relates to possible device quality?

A: The difference between the evaporation and chemical deposition is that the latter is very fluffy. Neither sticks too well, but I think this is caused by the  $\text{SiH}_4$  and may not be inherent to the CVD process by itself. I think there is some possibility of precluding the non-stickiness.

Q: Could you give a growth rate for CVD?

A: We use a rate of about one micron per minute.

Q: Did you make any cells from this material?

A: Next month, the sponsor and I are hoping to make junctions and that we will have a high temperature for diffusion.

Q: What did you say the sputtering rate was?

A: The sputtering rate we used was one micron per hour.

## GRAIN MODIFICATION IN POLYCRYSTALLINE SILICON SHEET FOR LOW-COST SOLAR CELLS

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### Presentation Summary

We describe here the approach suggested in a recent joint proposal for the achievement of appropriately large grains in polycrystalline silicon sheet. The purpose of developing such sheets is to meet the need for large area, low cost, moderate efficiency photovoltaic solar energy converters. It appears that at least one of the more successful methods for producing polycrystalline silicon sheets, i.e., electron beam evaporation, results in a grain size that is too small to obtain a reasonable conversion efficiency with a practical grid structure. The proposed project is to recrystallize the grains into larger ones by a strain-anneal technique. The essence of this process is to deform the material plastically by a small amount, and then heat treat it at an elevated temperature. This technique is not usually feasible with brittle materials, such as silicon at room temperature, because of fracture prior to plastic deformation. However, some brittle materials (NaCl, CaF<sub>2</sub>, MgO) have been recrystallized by strain-annealing at temperatures of about 0.5 and 0.6 times the melting point, respectively. Some plastic deformation has been observed in silicon (Refs. 1 and 2) at a temperature as low as 600°C. We propose to obtain our plastic deformation by bending the composite silicon-metal sheet around a mandrel at about 700°C. The annealing is to be carried out at 800° to 900°C. Both compression and tension deformation modes will be studied.

### References

1. J. R. Patel and A. R. Chaudhuri, *J. App. Phys.* 34, 2788 (1963).
2. W. D. Sylwestrowicz, *Phil. Mag.* 7, 1825 (1962).

### Discussion

**Q:** Have you actually been able to get any silicon to recrystallize under any experiment?

**A:** This is a proposal. We have not done any work, but I might say in that connection that there are, of course, intrinsic strains in the films whenever you put a film on a substrate, and the value of this intrinsic strain is about the same as you would get at the yield stress. Now there seems to be something different between the strains that are in the film as films, and this is a subject which is not well characterized in the literature theoretically, and the kind of strain that you put in plastically. Perhaps the plastic strain is less homogeneous and has some kind of a gradient, but it does seem to be more effective than just straight cold work.

**Q:** What is the thickness of the film you are talking about?

**A:** About ten microns of silicon onto, say, steel.

- Q: This work was also done on cadmium telluride and zinc selenide under a laser window program with the Air Force at Wright-Patterson, and, on those materials, it was found that although it worked, this was almost a hot pressing process, where you introduce the strain and then anneal in a hot pressing jig. They also found that although you could not increase the grain size substantially this way, the properties of the crystallites so formed were really not quite good enough for laser windows, for example. The question I wanted to raise was, do you have any idea what to expect the properties of the recrystallized crystals to be like?
- A: Not from a ceramic point of view such as you mentioned. The requirements for a laser window are more stringent than for our solar cells because of the application that the laser windows are being used for. I will say that the quality of the metal single crystals is quite high. I have done this with aluminum and have gotten 6 or 10 inches worth of crystal 1/16 inch thick and a bar of about three inches. And it is actually higher than I got at the time by, say, the Bridgemen method for growing a single crystal, but that is in metal.
- Q: In cuprous oxide, we have crystals 1 by 4 inches, which were not obtained by strain but from exaggerated grain growth. The exaggerated grain growth was carried out near the melting point. The strain method of growing large crystals is a rather delicate method as I understand and, normally, as you have indicated, it is done intentionally. In this case, if I understand what you are saying, the thin film was on a substrate and you will then remove the substrate, which leads to a very complex system of strain. Do you think that this is a good approach to strain annealing?
- A: I am not so sure I understand the complexities you refer to, but the film is very thin. In the bending of a beam, of course, the thin layer near the surfaces will be pretty much in pure tension. This is a cylindrical specimen being bent around the mandrel so that we feel that the film would be pretty much in pure tension and pure compression. Of course, around the edges where it is not being curved, you are going to have a variation because the radius is varying, but as long as you have a certain radius, you should get pure tension or pure compression. We visualize that if this were to work out, you could do this continuously with long sheets, and maybe then there would be no difference from one end to the other in the continuous process.
- Q: Could you tell us what grain size you will be starting with and what final size you are expecting?
- A: Well, we hope to be starting with perhaps a 1-micron grain size and ending up with a grain size of at least 10 microns; hopefully better.
- Q: How do you get the thing to fly again after it goes through this process? Is that a problem?
- A: No. You could visualize it as, say, going around a mandrel at a right angle. The substrate will have enough plasticity so it will start straight and end straight.
- Q: Have you ever tried just annealing at an elevated temperature on a flat substrate?
- A: I think this is part of the program that Professor Fang is presently engaged in.
- Q: Is some improvement expected to come out of this?
- A: I think he already mentioned some improvement in his previous talk.

## DEVELOPMENT OF LOW-COST THIN FILM POLYCRYSTALLINE SILICON SOLAR CELLS FOR TERRESTRIAL APPLICATIONS\*

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### Presentation Summary

The objective of this work is to develop low-cost thin film polycrystalline silicon solar cells suitable for terrestrial applications. Three work areas are involved: (1) the deposition and characterization of polycrystalline silicon films, (2) the preparation and characterization of p-n junctions and Schottky barriers, and (3) the fabrication and evaluation of thin-film solar cells.

The initial phase of this work has been directed to the deposition of polycrystalline silicon films on low-cost substrates by chemical vapor deposition techniques. Steel is by far the most economical choice for a substrate of large area, although many of its properties are undesirable. For instance, the linear thermal expansion coefficient of most low-cost steels is 3-4 times higher than that of silicon. Thus, the steel substrate used for the deposition of silicon should be of low hardness to minimize the effects of the large difference in thermal expansion coefficients. Also, carbon is soluble in iron, and the iron-iron carbide system undergoes complicated solid phase transformations. Therefore, the steel substrate should be essentially free of carbon to minimize the phase transformations in the substrate during the fabrication process. In this work, U. S. Steel Vitrenamel I and Armco silicon steel were selected as substrates.

To produce relatively large silicon crystallites, the chemical vapor deposition of silicon on steel substrates should be carried out at temperatures of 800°C or above. At these temperatures, however, silicon reacts with iron to form iron silicides. Thus, a diffusion barrier must be applied to the substrate surface to minimize the diffusion of iron from the substrate into silicon. The diffusion barrier must be compatible with steel and silicon in properties. The use of tungsten, titanium, silicon dioxide, and borosilicate as diffusion barriers was investigated; these materials can be readily deposited on steel substrates by chemical vapor deposition techniques. Tungsten was deposited on steel substrates by the thermal reduction of tungsten hexafluoride with hydrogen followed by the deposition of silicon using the pyrolysis of silane in the temperature range 750-1100°C. At 900°C or above, the deposit consists of large crystallites and appears to be epitaxial with respect to the substrate; however, its low electrical resistivity suggests the presence of iron silicide. The diffusion of iron is considerably reduced at 800°C or below, and the deposit was finely polycrystalline with a resistivity of less than 1 ohm-cm. Thus, tungsten is not entirely satisfactory as a diffusion barrier. Titanium deposited by the reduction of titanium tetrachloride with the substrate in a hydrogen atmosphere at 1000°C was also found to be unsatisfactory. Silicon dioxide deposited by the oxidation of silane and borosilicate deposited by the oxidation of a silane-diborane mixture have been used successfully as diffusion barriers. For example, silicon films of 50 μm thickness deposited on borosilicate on steel substrates were found to be n-type with resistivities of several hundred ohm-cm. The carrier concentration and mobility in these films are under study, and the control of carrier concentrations in silicon films is also underway.

The above results have been discussed in detail in Report NSF/RANN/SE/GI-38981/PR/73/3.

Slides 1 through 8 were presented at the NSF Workshop on Photovoltaic Conversion of Solar Energy for Terrestrial Applications.

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**Discussion**

- Q:** In the silicon single-crystal solar cell you have efficiency of around 12 to 14 percent; in the polycrystalline cell you might allow 6 or 8 percent. Can you give a breakdown of how much loss in the latter is due to fill factor change, how much is due to short-circuit current, and how much due to open-circuit voltage?
- A:** I have read through the literature to some extent concerning the efficiency of the solar cell fabricated from a polycrystalline ingot. The latest one I could find claimed 6 percent efficiency. I noticed the grains could be as large as several millimeters. However, I cannot give you a breakdown on what percentage of the decreasing efficiency is due to grain boundaries or due to other factors.
- Q:** Does it reflect the grain size of the substrate?
- A:** When you use tungsten for the diffusion barrier at high temperatures, the grain size in the deposit is more similar to the grain size in the substrate. In the case of silicon steel, we took a grain size of the order of several centimeters. However, the deposit was contaminated by iron. When we used borosilicate as diffusion barrier, there was no iron contamination. In other words, borosilicate is amorphous just like silicon dioxide. Therefore, the grain size of a deposit of silicon is considerably less. We have probably 40 to 50 microns in grain size in the 50-micron-thick silicon layer.
- Q:** What is the reason that you insist on metals as substrate?
- A:** Because of the cost. We have looked into ceramic materials such as aluminum oxide. Ceramic materials are very rigid structurally and when we deposit silicon or other materials with a somewhat different expansion coefficient, the deposit cracks off easily. In the case of steel, because of its softness, you can allow some differences. With a borosilicate as a diffusion barrier, you can also "buffer" the difference in the thermal expansion coefficient.
- Q:** Have you made some cells on these?
- A:** We have not made cells. I hope in the very near future we can produce p/n junctions.
- Q:** Have you seen some results on cells?
- A:** Yes. The results I quoted were from the literature.
- Q:** What was the open-circuit voltage and the short-circuit current?
- A:** In the case of the polycrystalline silicon cell fabricated in 1961, I believe that the open-circuit voltage was approximately 0.25 to 0.30 volts.

1. From ingots: large grains obtainable  
 fabrication cost similar to single crystal cells  
 efficiencies up to 6%, depending on grain size
2. From films: selection of substrate important  
 low fabrication cost  
 efficiency up to 0.9% for 1 cm<sup>2</sup> cell  
 [Heaps et al., IEEE Trans. Electron Devices,  
ED-8, 560 (1961)]

Slide 1. Polycrystalline Silicon Solar Cells

Task	Months								
	2	4	6	8	10	12	14	16	18
1. Deposition and characterization of silicon films on steel substrates.	▬								
2. Preparation and characterization of p-n junctions.			▬						
3. Fabrication and characterization of Schottky barriers.			▬						
4. Fabrication and characterization of solar cells.					▬				
5. Cost analysis of deposition and fabrication processes.						▬			

Slide 2. Program Plan for Thin Polycrystalline Silicon Solar Cells



Fe(l)  $\xrightarrow{1534\text{ }^\circ\text{C}}$   $\delta$ -Fe (bcc)  $\xrightarrow{1404\text{ }^\circ\text{C}}$   $\gamma$ -Fe (fcc)  $\xrightarrow{900\text{ }^\circ\text{C}}$   $\alpha$ -Fe (bcc)  
 Small volume changes associated with phase changes. The thermal expansion coefficient of iron and most steels is 3-4 times higher than that of silicon. Substrates should be soft to minimize the effects of large differences in thermal expansion coefficients.

Iron forms solid solutions with carbon and complicated solid phase transformations exist in the Fe-Fe<sub>3</sub>C system. Substrates should be essentially free of carbon.

Iron forms several silicides, and siliconization of iron takes place at temperatures below 800 °C. Diffusion barriers are therefore required when silicon is prepared by chemical vapor deposition.

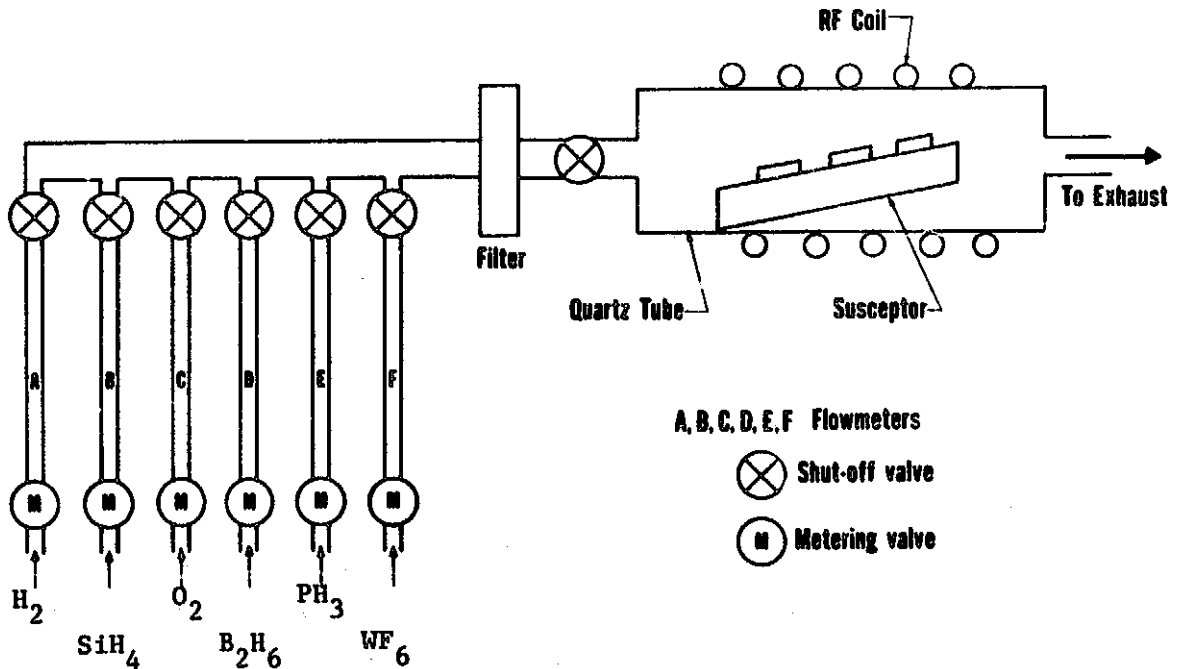
Slide 3. Properties of Iron and Steel

	Armco Si Steel	USS Vitrenamel I	Silicon
Composition	2.84% Si, 0.11% Mn <0.001% C	0.008% C	
Thermal Expansion (10 <sup>6</sup> °C <sup>-1</sup> )	12 - 15 (RT - 1000 °C)	(13-14) x 10 <sup>6</sup> °C <sup>-1</sup> (RT - 800 °C)	4
Grain size	> 1 cm [001] direction parallel to rolling direction	millimeter size obtainable after annealing	
Hardness (Moh scale)		3	7

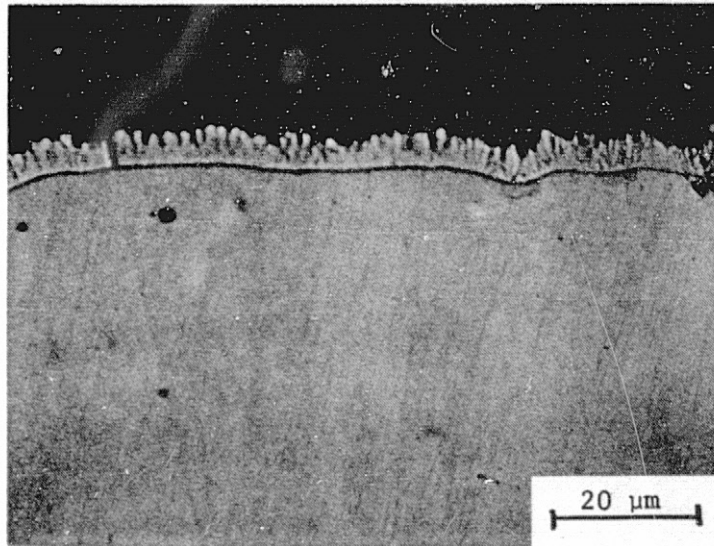
Slide 4. Properties of Steel Substrates for Silicon Deposition

Silicon	$\text{SiH}_4(\text{g}) \rightarrow \text{Si}(\text{s}) + 2\text{H}_2(\text{g})$
	$\text{SiHCl}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{Si}(\text{s}) + 3\text{HCl}(\text{g})$
Tungsten	$\text{WF}_6(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{W}(\text{s}) + 6\text{HCl}(\text{g})$
Titanium	$\text{TiCl}_4(\text{g}) + 2\text{Fe}(\text{s}) \rightarrow \text{Ti}(\text{s}) + 2\text{FeCl}_2(\text{g})$
Silica	$\text{SiH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{g})$
Borosilicate	$x\text{SiH}_4(\text{g}) + y\text{B}_2\text{H}_6(\text{g}) + (2x+3y)\text{O}_2(\text{g}) \rightarrow$ $(\text{SiO}_2)_x(\text{B}_2\text{O}_3)_y(\text{s}) + (2x+3y)\text{H}_2\text{O}(\text{g})$

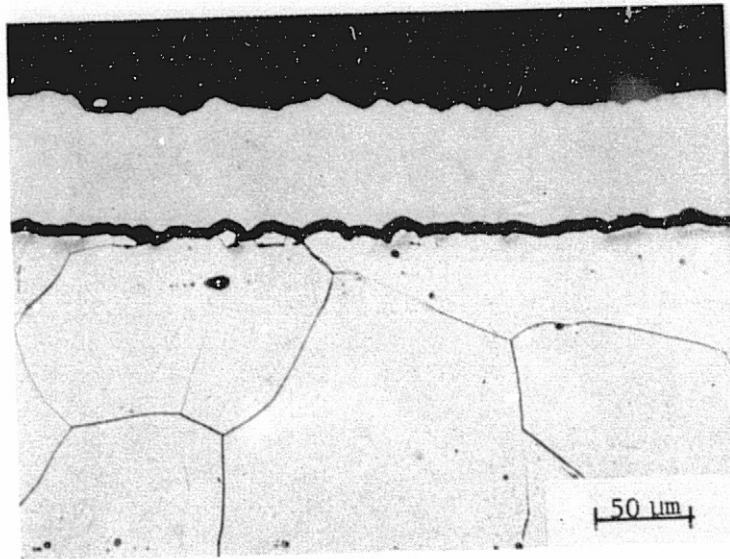
Slide 5. Deposition of Silicon and Diffusion Barriers



Slide 6. Growth Apparatus for Polycrystalline Films



Slide 7. Vertical section of a silicon-tungsten-steel specimen obtained by the successive deposition of  $5\ \mu\text{m}$  tungsten and  $5\ \mu\text{m}$  silicon on U.S. Steel Vitrenamel 1. Tungsten is effective against the diffusion of iron from the substrate into silicon only at deposition temperatures below  $800^\circ\text{C}$ .



Slide 8. Vertical cross section of a silicon-borosilicate-steel specimen obtained by the successive deposition of  $5\ \mu\text{m}$  borosilicate and  $55\ \mu\text{m}$  silicon on U.S. Steel Vitre enamel 1. Borosilicate is an effective barrier against the diffusion of iron from the substrate into silicon. The silicon is n-type with a resistivity of about  $400\ \text{ohm-cm}$ .

## FABRICATION OF LOW-COST THIN FILM SOLAR CELLS

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### Presentation Summary

#### I. Introduction

The purpose of this note is to describe an approach to fabricating thin film photovoltaic devices. The approach is based on using a heterojunction CdTe-CdS device developed by Battelle-Frankfurt Laboratories, combined with a unique high-rate sputter-deposition technology developed by Battelle-Northwest Laboratories, which may allow sequential, automated, single-environment deposition of the device elements. It is assumed that practical, economically competitive solar energy generating systems can be realized only by inexpensive fabrication of low conversion efficiency devices. A number of the processes presently used in making thin film photovoltaic devices are not amenable to automation. However, if thin film solar cells are ever to be considered for terrestrial application, it appears imperative to develop a single-environment fabrication technology. Therefore, in the following discussion, an all-vacuum approach is suggested, and is used as the basis for generating the projected costs.

It is also visualized that any fabrication development is parallel to more basic device technology development, but that the basic development is guided by what exists or can reasonably be projected in the fabrication technology.

#### II. Basic Approach and Costs

##### A. Cell Structure

It is visualized that the converter consists of a 5- or 6-element structure as indicated in Fig. 1. The materials suggested are only used for illustration, since the total material system, of course, will be subject to definition. The individual cell size will be a defined optimum and each individual cell is visualized to be interconnected resulting in a subpanel size of 1 ft<sup>2</sup>. It is difficult at present to suggest a deposited interconnection scheme, but various strip and wire bonding schemes may be considered drawing on the techniques used in the semiconductor technology. Therefore, the elementary cost calculations which follow are based on producing a subpanel of 1 ft<sup>2</sup>.

##### B. Basic Data

The solar constant (average distance from sun) at the edge of the earth's atmosphere is taken to be 137 mW/cm<sup>2</sup>. The maximum radiant solar power density at the earth's surface (sea level) on a bright clear day is normally listed as 108 mW/cm<sup>2</sup>. Then assuming an efficiency of 10 percent, which is slightly higher than the obtained efficiency of 7 percent reported by Clevite, the peak power output will be:

$$P_{\max} \approx 10 \text{ mW/cm}^2$$

Therefore,

$$P_{\max}/\text{ft}^2 \approx (12 \times 2.54)^2 \times 1 \times 10^{-2} \approx 9.3 \text{ PW/ft}^2$$

The estimates of power cost are based on the peak watt (PW) value. Assuming an Arizona location, however, the average power output would be approximately 2 W/ft<sup>2</sup>, which would give more realistic estimates of power cost.

### C. Deposition Data

The estimates of deposition rates and power requirements are based on data from existing computer controlled batch systems. It is assumed that all deposits are sequentially sputtered deposits, which may in reality be changed to a combination of evaporation and sputtering. In that case the power estimates are probably on the high side. Deposition rates of  $1 \mu\text{m}/\text{min}$  have been demonstrated for some dielectric materials, and several  $\mu\text{m}/\text{min}$  deposition rates have been demonstrated for many metals. The power requirements for depositing the total structure on a square foot panel is estimated to be 33 kW-hr.

### D. Power Cost

Labor, materials, overhead and G & A were estimated from experience with existing systems. Each automatic, sequential deposition system was estimated to cost \$300K with capability of producing 288 subpanels/day ( $1 \text{ ft}^2$ ). These systems were amortized over a period of 5 years. Using such values the estimated cost per panel is about \$4.40/panel resulting in a power cost of \$0.47/peak watt.

### III. Brief Discussion

The abrupt CdTe-CdS heterojunction device demonstrated by Battelle-Frankfurt Laboratories did show an efficiency at room temperature of 5 percent to 6 percent under simulated solar light of  $50 \text{ mW}/\text{cm}^2$ . Work thus far has indicated that further development is needed to obtain higher conductivity in the P-layer and to improve the contact to that layer. Both the structure and the materials involved in this system are compatible with the proposed deposition approach.

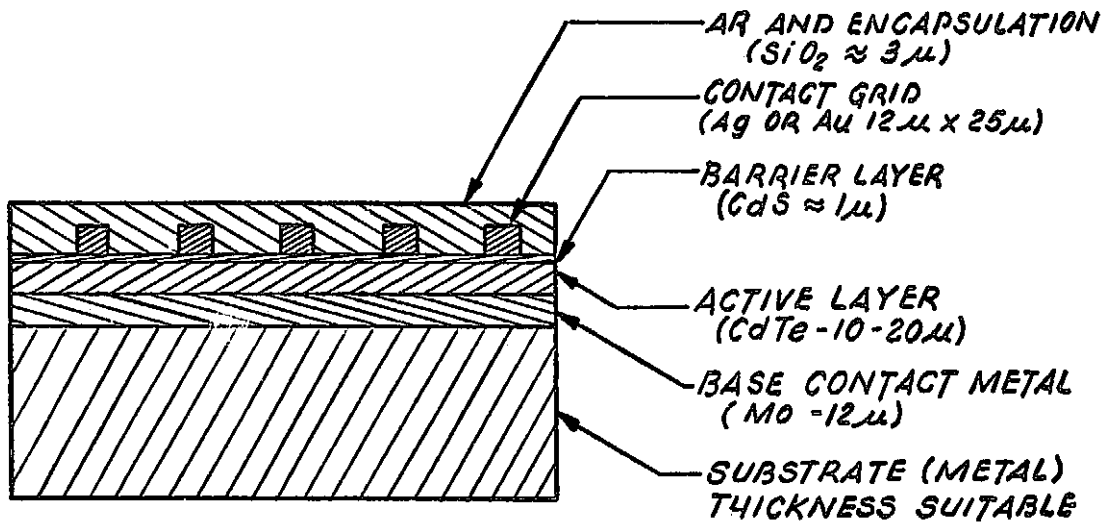
A fully automated, numerically controlled deposition technology has been developed at Battelle-Northwest Laboratories over the last six years. Such systems have now been operated over several years for deposition of a wide variety of materials and with demonstrated deposit reliability and reproducibility. Deposition rates of about 0.25 mm per hour have been achieved with certain materials and scale-up to 0.5 mm/hour is feasible. Deposit thicknesses have ranged from a few hundred Å to 1.25 cm. The high rates are important if manufacturing time is to become reasonable.

### Discussion

- Q: What is the technique?
- A: It is a supported-discharge sputtering technique.
- Q: What does that mean? What is different about this?
- A: It means very high power densities at the target. How do you get it? You have two things to play with: You have lots of ions and you have energy to play with – energy of the incoming ions. And primarily, here, we are dealing with creating lots of ions.
- Q: Does your energy replacement time of 640 days allow for the energy used in extrapolating and purifying the raw materials?
- A: No, it does not.
- Q: What kind of cell did Robinhorst and Bonnet make on which they reported 6 percent efficiency.
- A: P-type cadmium telluride and n-type cadmium sulfide, and the p-material was essentially a modified CVD-deposited material and the cadmium sulfide was vapor-deposited.
- Q: Do you think this can be adapted to silicon?
- A: To silicon? I have not suggested it. I had said earlier that I don't really belong in this section.

Q: You are saying that you can get similar results by sputtering?

A: No. I said we haven't experimented with these material as yet. We do have plans to begin working on these under ARPA sponsorship. But this is for laser mirror application.



NOTE: MATERIALS AND THICKNESSES ARE FAIRLY REALISTIC BUT PRIMARILY FOR ILLUSTRATION DRAWING NOT TO SCALE

Fig. 1. Typical Cell Structure



## LOW-TEMPERATURE POLYSILICON

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### Presentation Summary

Characterization of polysilicon has become of considerable interest due to its potential application in many areas of the electronic industry. However, characterization seems to be limited to resistivity and growth rates. If polysilicon is to be of use in photovoltaics, then other properties, such as minority carrier diffusion length and grain size, are among those which are of interest. Further, if the product is to be of low cost, then the process techniques which are used to develop the material and device characteristics must also be of low cost, which includes effort and energy.

### Device Characterization

As shown in Fig. 1, the device is divided into six layers each of which has its individual contributing function and must have certain characteristics.

- (1) **Substrate.** The substrate must have good mechanical strength and rigidity to support the silicon and maintain its basic continuity. Its thermal expansion coefficient should be close to that of silicon. It must be capable of good electrical contact to the silicon and other interconnections with the electrical circuit. Its thermal conductivity should be good to insure removal of heat from the silicon and, perhaps, transfer to thermal storage. It should be of low cost and readily available.
- (2) **Rear contact interface.** The basic character of this interface should provide good ohmic contact for the majority charge carriers and have blocking characteristics for the minority carriers. Good optical reflection properties would decrease the necessity for a thick layer to insure adequate generation of charge pairs.
- (3) **Polysilicon base layer.** This layer should have moderate resistivity (one ohm-cm) to insure adequate diminishing of the grain-boundary effects. Lower resistivities may diminish achievable bulk-like properties.
- (4) **Emitter.** A graded impurity concentration would diminish the effects of surface recombination and increase collection from shorter wavelengths. Its resistivity should be sufficiently low to insure easy tunneling across grain boundaries to the contact areas.
- (5) **Emitter layer contacts.** These contacts should be of low resistivity and should not contribute to grain-boundary faulting.
- (6) **AR coating.** Consideration in the choice of this coating should be given to providing protection against atmospheric contaminations in addition to its anti-reflection properties.

Each of these layers has a unique set of problem areas which impose certain limitations on the others. The areas we will concentrate on here are those of substrate and base.

### Substrate

A number of possible substrates exist. However, suppose, for example, that we choose aluminum. It is plentiful and of relatively low cost. Some of the properties of aluminum and silicon are shown in Table I. There are at least two critical properties which relate to the silicon-aluminum interface. These are the coefficient of thermal expansion and the eutectic temperature. If polycrystalline silicon is to be grown at this interface, then the temperature

must be below 577°C. This temperature is not far below the melting point of aluminum, 660°C. It would seem that little is to be gained by attempting to gain access to this temperature interval; however, the resistivity of deposited polycrystalline films has been shown to increase abruptly in the neighborhood of 600°C (Ref. 1). Similar results have been noted at a temperature of 530°C using Ar or N<sub>2</sub> (Ref. 2).

Under the assumption that eutectic-melting point problem with aluminum can be avoided, there are other questions which bear answering. It has been known for some time that aluminum metallurgy results in etch pits when the contacts are removed (Ref. 3). The precise cause and process by which this situation results is not well understood, but apparently results from the affinity of silicon for aluminum and vice versa (Ref. 4).

It is also suggested that the rear contacts should result in p<sup>+</sup> impurity profiles. These profiles should act as minority carrier blocking contacts and reduce ambipolar diffusion and contact recombination. The result is a larger concentration of minority carriers in the base region which increases the open-circuit voltage.

#### Silicon Base Layer

Growth of polycrystalline silicon at temperatures in the neighborhood of 600°C has been accomplished (Refs. 1 and 2). Resistivities for these films have been reported as being quite high. These resistivities are usually "in-plane" measurements which result in resistivities considerably larger than those for bulk silicon. One of the contributing causes is the grain-boundary potential barrier. Another is carrier removal by the grain-boundary.

Films grown with B<sub>2</sub>H<sub>6</sub> resulted in lower resistivities following heat treatment above 1000°C. The times and temperature were out of proportion for a Si-Al interface.

To reduce the effects of grain boundaries, the grain impurity concentrations must be of the order of 10<sup>16</sup> cm<sup>-3</sup>. This concentration will satisfy the charge requirements of the grain boundaries and reduce the grain Debye length to a magnitude which permits the greater portion of the grain to have bulk properties. A secondary effect is a reduction of the grain boundary influence on recombination.

The interior of each grain is surrounded by an electron potential barrier. The base is p-type; this barrier will inhibit conduction between grains. A p<sup>+</sup> substrate contact will inhibit minority carrier flow out of the back contact. Diffusion of majority carriers across the pn junction will inhibit electron removal at the junction.

Growth of the emitter layer should be accomplished such that the layer has a low resistivity, inhibits shorting via grain boundaries, and does not preferentially assist collection of generated carriers in the grain boundaries.

#### References

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#### Discussion

Q: What method do you plan for low-temperature growth, the CVD method?

A: CVD was all we planned to use.

- Q: What kind of deposition rate do you expect at 600°C? What is the highest doping concentration that you can incorporate at this temperature?
- A: What is the high doping concentration? Doping concentration does not seem to be a problem. The literature contains quotes of  $10^{19}$ ,  $10^{20}$  at that temperature. Rates typically would be 0.01 microns, but if you use the right carrier, you apparently can increase this by approximately an order of magnitude and perhaps greater. That is one of the problems that has to be investigated.
- Q: Can you characterize the grain boundary problem in more detail - chemical composition, electrical properties, etc.?
- A: Normally, a grain boundary causes the energy band to bend up so that it would become more highly p-type, i.e., it tends to become a shorting path. Now if you have a long grain, this essentially means that its resistivity is going to be somewhat lower than the resistivity of the bulk for the case of a bulk resistivity in the range of 1 ohm-centimeter or maybe 0.1 ohm-centimeter. So it tends to short even to the base layer. You can eliminate that somewhat by decreasing the resistivity, but not completely. What kind of impurities go into it? There are many states, of course. It does become charged and that is why it bends up.
- Q: You said you had to keep the diffusions and the contacts away from the grain boundaries. Is that right?
- A: Somehow I think you would have to isolate these, otherwise I think they would tend to short.
- Q: Do you have any idea how you are going to isolate them?
- A: That is one of the problems that we have to tackle. We tossed around the concept of an oxidation technique, but I'm not certain that would really isolate the grain boundaries.

Table I. A Comparison of Certain Physical Properties of Aluminum and Silicon

Property	Aluminum	Silicon
Density, g/cm <sup>3</sup>	2.7	2.33
M.P., °C	660	1410
Eutectic P, °C	577	
Thermal expansion	15.1	2.5-3.5
Specific heat, cal/g	0.215	0.169
Dielectric constant	1	12
Index of refraction	1	3.5
Coeff. of absorptions of solar radiation	0.15	

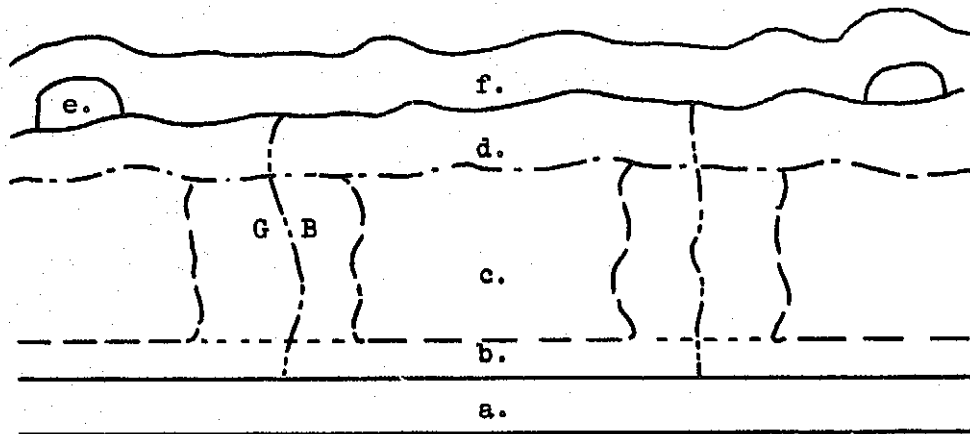


Fig. 1. Six-Layered Structure: a. Substrate, b. Substrate-Poly Interface, c. Polysilicon Base, d. Emitter, e. Emitter Contact, f. AR Coating

## **POLYCRYSTALLINE SILICON SOLAR CELLS: THE CENTRALAB-DOW CORNING PROGRAM**

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### **Presentation Summary**

A tenfold reduction in present silicon costs can be obtained by using polycrystalline silicon as a starting material for terrestrial solar cells. A further fourfold reduction can be obtained if all shaping and slice preparation operations are eliminated by using polycrystalline thin films (around 10  $\mu\text{m}$  thick).

The polycrystalline process presently used provides silicon below \$60.00 per kilogram, and it is already being operated at high volume production.

For a thin-film cell 10  $\mu\text{m}$  thick with a conversion efficiency of 0.5% and using the \$60.00 per kilogram price, the cost of silicon alone in the cells can be reduced to around \$300/kW of delivered power with a corresponding value of \$3.00 per meter<sup>2</sup>.

These costs can be further reduced if the conversion efficiency can be increased without adding much complexity to the film formation process.

Preliminary tests using thick slices of Dow Corning polycrystalline silicon have resulted in cells with conversion efficiencies approaching 1%, using essentially the present cell processing methods. These cells had limitations which could be ascribed directly to the grain boundary properties. These properties result in a low effective carrier lifetime, because of recombination at the grain boundaries, and excess leakage currents caused by several known characteristics of grain boundaries.

The lowered lifetime reduced the current by a factor of three, while the excess currents reduced the voltage, and in combination with the lateral resistance of the grain boundaries gave low curve fill factor.

The proposed program is intended to study thin polycrystalline silicon films and cells made from these films. Slices cut from polycrystalline chunk material will be used for detailed study of grain boundary effects to help optimize the thin film properties.

The program includes several phases as follows:

- (1) To grow polycrystalline silicon films using a range of deposition conditions, to optimize and control the grain size and other film properties.
- (2) To evaluate several substrates which allow good film properties to be obtained and which are suitable for subsequent cell processing. These substrate materials will include both metals and insulators.
- (3) To modify the film properties during growth, by incorporating impurities both in the grain boundaries, and also inside individual crystallites with the goal of controlling the carrier lifetime and resistivity.
- (4) To modify the as-deposited silicon, to reduce the effects of grain boundaries (remedial measures).

- (5) To evaluate the polycrystalline silicon,
- a. For grain boundary properties
  - b. For transverse and normal resistivities
  - c. In small area diodes (particularly to measure excess currents)
  - d. In solar cells of large area (to measure  $I_{SC}$ ,  $V_{OC}$ , curve fill factor, series resistance, and diffusion length)
- (6) To evaluate some novel solar cell structures, more suited to the thin films.

The results obtained on the cells and diodes will be analyzed and related to the film properties. This information will be fed back to the silicon group to help in formulating deposition procedures for producing improved films in subsequent runs.

The goals of this program can be summarized as follows:

- (1) To determine the main features of polycrystalline silicon which have the greatest effect on solar cell performance—a sort of figure of merit for polycrystalline silicon.
- (2) To prescribe the correct growth conditions, or post-growth treatments which will improve cell performance without adding substantially to the cost of silicon.
- (3) To design a cell structure and processing sequence which will provide best cell output from the optimized polycrystalline silicon, and to fabricate some state-of-the-art cells.
- (4) To extract realistic cost estimates for larger scale cell production.

### Discussion

Q: Would you indicate how you are going to reduce the effects of grain boundaries?

A: Yes. We would like to introduce some doping to discourage carrier recombination at the grain boundaries. We believe that we have ways of taking them out of consideration when using a diffused junction, which we realize is not the ideal case. The tests to date have shown that grain boundary diffusion is not as highly enhanced as the literature led us to believe, so that even with diffusion or other methods of forming a junction, we feel that there are practical ways — sequence process ways — where you do not have the grain boundaries and their associated space-charge regions, which act as critical areas in the cells.

Q: Even though you are getting one to two percent conversion efficiency, we are finding that the cell is still highly stable. Something like 200 to 300°C is needed to really destroy the characteristics. Do you find similar results?

A: You mean stable in operation after being made?

Q: After you made it, it has a very stable characteristic.

A: We don't heat them up 200°C, but they certainly last a few months. They seem to be a fairly well-characterized bad cell.

Q: But the point is still to be made that the cell is stable, even though it has a very disorganized structure.

A: Yes. People ask why we don't use cadmium sulphide, with which we can already get three or four percent with polycrystalline material. We feel that silicon has some advantages, and it has some possibility of being improved to make it competitive.

**Q:** What were the grain sizes? And, can they vary that as they grow the poly?

**A:** They can vary it if you give them a choice of substrates. If they can use an insulating substrate, they can run their CVD process at high temperatures and at rates sufficient to give large grains. We feel, like most people, that if the grain diameter is of the order of a tenth or maybe a fifth of the thickness, that we've got a sporting chance, first of all to modify the bulk silicon so that we don't have to rely strictly on diffusion of carriers over that fairly small distance, and to try to reduce the effectiveness of the grain boundaries in the recombining of carriers. We didn't measure the grain size, but they were very small grains. A rough estimate is that they are in the neighborhood of one to 500 microns.

**Q:** About the grain boundary treatment again, have you considered differential diffusion of oxygen to achieve differential grain boundary oxidation, and therefore, to achieve electrically isolated structures?

**A:** Yes. We have also considered preferential diffusion of impurities other than oxygen, but we haven't done any of them yet.

**Q:** What is the lifetime you measured on these layers?

**A:** Our short-circuit current (air mass zero) went down to about 30 percent of its normal value. We have measured diffusion lengths of the order of one to three microns. That is a lifetime of  $10^{-7}$  or  $10^{-8}$  seconds a low lifetime and compatible with what other people have mentioned. We lose about one-half to two-thirds of our current collection, due principally to the large effect of grain boundary recombination.

## PROPOSAL FOR LOW COST SILICON PROCESSES

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### Presentation Summary

Many investigations have been made into the cost of solar array assemblies. Figure 1 shows a quick analysis of the silicon materials cost per watt based on the assumption that the arrays will be made from typical 2-inch wafers with very loose specifications on wafer parameters. Even with these loose specifications it is clear that to obtain energy costs in the \$0.5 per watt range that the silicon materials cost must be reduced by more than one order of magnitude.

In recognition of this necessary reduction in materials cost the National Center for Energy Management and Power at the University of Pennsylvania and Dow Corning have proposed to study methods and techniques designed to (a) reduce the cost of the basic polycrystalline silicon, (b) reduce the cost of converting this silicon into large singular sheets, and (c) combine these into a continuous system for the fabrication of integrated silicon solar arrays.

The primary objective here is to describe the efforts proposed by Dow Corning for the reduction of the basic polycrystalline silicon costs. The main goal would be to provide polycrystalline silicon suitable for subsequent solar cell fabrication in the price range of less than or equal to \$6 per kilogram which is a reduction over the present costs by a factor of ten.

The basic starting point for such a study is with the present process which involves:

- (a) Reduction of silica by coke to yield metallurgical-grade silicon at an approximate price of \$0.5 per kilogram.
- (b) Pulverization and reaction in a bed fluidized by  $\text{HCl}$  to form chlorosilanes.
- (c) Distillation to fractionate trichlorosilane from other chlorosilanes.
- (d) Further distillation to purify the trichlorosilanes.
- (e) Hydrogen reduction of trichlorosilane to form silicon at high temperatures by normal CVD techniques.

This semiconductor grade of silicon costs more than 100 times that of metallurgical-grade silicon and has doping and heavy metal impurity levels in the sub parts per billion range. There are techniques that could be used to reduce the cost of transforming metallurgical-grade silicon into usable solar cell-grade silicon by the present CVD techniques based on large volume and reduced purity requirements. For example, reduced distillation, reactor optimization without regard to purity and adoption of large volume processing steps could all be used to reduce the cost of present-day silicon. The total effect of all these changes would probably reduce the cost of poly silicon to no lower than \$30 per kilogram (Ref. 1).

The result of this reduction would still put poly silicon costs at \$0.50 to \$0.60 per watt (Fig. 2) which is yet more than a factor of five too high. Thus, it is apparent that optimization of the present process is not sufficient, and we do, indeed, need a new silicon production technology to obtain bulk silicon at a sufficiently low cost.

Dow Corning's objective in the proposal with the University of Pennsylvania are shown in Fig. 3. There is available in the literature today, several techniques that have been tried and suggested for obtaining silicon (Ref. 2). In many cases these techniques were abandoned because they did not provide semiconductor-grade silicon and/or the



materials technology at that time was not sufficient to take advantage of possible processes. In addition, the present University-Industry team has proposed new processing techniques. There may also be CVD techniques not based on the present process which can be used to provide the necessary silicon. In any case, a rating system will be developed which will effectively compare one process against another. The criteria to be used in this rating are shown in Fig. 4.

Of obvious concern is that the silicon purity be sufficient to provide 1.0 ohm-cm material with lifetimes in excess of 1  $\mu$ sec. The question of whether or not the needed quantity of silicon can be made from available resources must be answered. The energy requirements must be such that it could be recovered within a very few years (<5 years). In addition the process must be compatible with the surrounding environment and with the concurrent developing sheet forming and integrated solar array programs at the University of Pennsylvania.

The experimental program will allow for attainment of data necessary to effectively rate one process against another. Also it will show experimental feasibility of the most promising silicon manufacturing processes that emerge from the prior rating and selection steps.

The main result of this technical effort will be Dow Corning's recommendation as to the two most favorable manufacturing processes for producing solar cell-grade silicon for large integrated arrays. Dow Corning will also provide a critique of the other considered silicon processes such that future process comparisons can be made when new technologies emerge.

Possible process technologies are shown in Fig. 5. Because there is a factor of 10 between the metallurgical silicon cost and the final necessary silicon cost we can consider upgrading this material directly. Here we can learn from other materials manufacturing industries, like the steel industry. Transport processes using silicon halide species can be used where these species are used to transport silicon continuously from a solid to gaseous form, and finally to deposition. Other process techniques would be to go directly to sand ( $\text{SiO}_2$ ) and convert directly into silicon via intermediate compounds. There is also available several silicates (e.g., fluorosilicates) which could be used in the electrolysis of molten salt mixtures to silicon.

Figure 6 shows the proposed long-range development of a low-cost silicon process. The present proposal is concerned with the first three-year period. Assuming initial success, it is anticipated that a low-cost silicon process could be commercialized within 10 years.

In summary, it is obvious that there are several potential silicon processes and it is necessary that these potential processes be rated and compared with one another to find the most favorable one necessary to provide the lower cost silicon required for the successful attainment of low cost silicon solar cells.

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## Discussion

**Q:** How do you arrive at dollars per watt from dollars per kilogram?

**A:** I assumed that a typical 2-inch slice today requires about 5 grams of polysilicon after the slicing, assumed the costs of crystal growth, yield factors, and assumed a conversion efficiency of about ten percent, all amounting to about a dollar per watt. You need to remember you've got a different number.

- Q: I've got the Currin, Ling, Ralph, Stirn paper from the last conference.
- A: Well, my cost is today, and that paper is future.
- Q: They were talking about today's process working from polycrystalline silicon, 14 cents a watt, \$140 per kilowatt. Now am I reading it wrong?
- A: I don't know. It doesn't sound right.
- Q: Fifty dollars per kilogram for the poly and \$340.00 a kilowatt?
- A: I don't know on what assumption it was derived.
- Q: It says a 4-mil wafer assuming 10 percent efficiency.
- Q: In that paper, material cost was at least 80 percent, so that a 4-mil thickness is quite significant when you are comparing these two.
- Q: I think one difference may be that in the original paper there was no loss considered in converting the poly into single-crystal silicon and then into a solar cell. You would have \$140.00 a kilowatt. The calculation here assumes present-day losses in this process – upward of 100 percent loss.

. ASSUME	50 MM SLICE 10 MIL THICK
. POLY NEEDED	3.5-5 GRAMS
. POLY COST	6¢/GM 21-30¢/SLICE
. WAFER COST	60-80¢/SLICE
. ENERGY	0.2 WATTS/SLICE
	POLY COST = \$1.00-\$1.50/WATT
	WAFER COST = \$3.00-\$4.00/WATT

Fig. 1. Present Polycrystalline Silicon Costs Per Watt

<u>MAXIMIZE PRESENT PROCESS</u>	
. LOWEST POLY COST	3-4¢/GM
. THINNER SLICES	4 MIL
. BETTER YIELD	40-50%
. POLY NEEDED	2.5-3.5 GRAMS/SLICE
. ENERGY	
	POLY COST \$0.50-0.60/WATT
THUS: NEW SILICON TECHNOLOGY NEEDED	

Fig. 2. Potential Lower Limit for Polycrystalline Silicon Costs with Present Process

### DOW CORNING OBJECTIVES

- ESTABLISH CRITERIA AND RATING SYSTEMS BY WHICH PAST, PRESENT, AND PROPOSED METHODS OF PREPARATION CAN BE COMPARED.
- OBTAIN DATA NECESSARY TO EFFECTIVELY RATE ONE PROCESS AGAINST THE OTHERS.
- EXPERIMENTALLY PROVIDE A FEASIBILITY DEMONSTRATION OF PROMISING PROCESSES.
- RECOMMEND THE TWO MOST FAVORABLE MANUFACTURING PROCESSES FOR PRODUCING SOLAR CELL GRADE SILICON.
- PROVIDE A CRITIQUE OF OTHER PROCESSES, LISTING THEIR STRENGTHS AND WEAKNESSES FOR FUTURE COMPARISONS WHEN NEW TECHNOLOGIES EMERGE.

Fig. 3. Dow Corning Objectives Under Present Proposal

### CRITERIA FOR PROCESS SELECTION

- QUALITY
- QUANTITY
- FEASIBILITY
- ENERGY REQUIREMENTS
- ENVIRONMENTAL EFFECTS
- RESOURCE AVAILABILITY
- ECONOMICS
- COMPATIBILITY WITH SUBSEQUENT PROCESS STEPS

Fig. 4. Criteria for Rating System

- POSSIBLE PROCESSES
- . UP GRADE SILICON FROM FERROSILICON PROCESS
  - . TRANSPORT PROCESSES
  - . CVD TECHNIQUES
  - . DIRECT FROM SAND ( $\text{SiO}_2$ )
  - . FLUOROSILICATES

Fig. 5. Possible Silicon Manufacturing Processes

- MILESTONES
- (COMPATIBLE WITH SUBSEQUENT DEVELOPMENT)
- 1974-1976: RATING AND SELECTION COMPLETED
- 1977-1979: SCALE UP AND PILOT PLANT OPERATION OF INDEPENDENT OPERATIONS
- 1980-1983: DEVELOPMENT OF CONTINUOUS PILOT PLANT
- 1984: COMMERCIALIZATION

Fig. 6. Long-Range Milestones for the Development of Low-Cost Polycrystalline Silicon

## SELECTIVE SURFACES FOR PHOTOTHERMAL SOLAR ENERGY CONVERSION MANUFACTURED BY CHEMICAL VAPOR DEPOSITION

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### Presentation Summary

This project will support research on a new approach to a selective solar energy converter that can be used to transform solar radiation into high temperature heat. This heat can be transferred and applied in a steam turbine-generator unit to produce electricity. The selective solar energy converter is basically a two-layered construction in which the top layer is a semiconductor material, such as silicon, having high absorption for solar radiation and high transparency for blackbody radiation from the heated unit. The bottom layer is a metal film having high reflectance.

A second significant feature of this project is the use of chemical vapor deposition (CVD) techniques for applying semiconductor materials for optical structures. The objective of the project is to adapt the CVD process to the fabrication of multilayered semiconductor coatings, to demonstrate the fabrication of semiconductor absorber-type optical coatings, and to measure the physical characteristics and the optical performance of these coatings as a function of temperatures up to 500°C.

Research during the period covered by this report centered on the interface between the silver reflector and the silicon absorber. Previous studies had established that the thin silver film agglomerated at the temperature of the silicon CVD deposition. In order to eliminate this basic problem in the fabrication of the converter stack, an agglomeration inhibitor was developed. Silver films thus stabilized withstand temperatures of up to 800°C without deterioration of their infrared reflectance.

Further refinement of the CVD process resulted in the deposition of 2- $\mu$ m thick silicon films of satisfactory optical quality onto the metallized substrate. For this part of the stack, the measured reflectance spectrum agrees well with the performance calculated under the assumption of IR-transparent silicon and undegraded silver reflectance.

Preliminary results of annealing studies show that no degradation of the optical performance of the absorber-reflector stack occurred after 150 hr. anneal at 540°C.

The results available at the end of this period can be interpreted as proof for the basic feasibility of the approach using the silicon-on-silver converter. The agreement between measured and calculated optical properties indicates that the predicted performance of the entire converter stack can be obtained once the silicon absorber carries the antireflection layer.

### Discussion

- Q: Why does putting the silicon on a reflecting surface prevent the infrared from being radiated?
- A: Five-micron silicon has negligible emittance in this range—it is thickness proportionate—and so the emissivity of the system is determined by the silver layer underneath. Our standard test is to run the solar substrate before and after silicon deposition. There is very little difference in reflectance between the two, meaning the silicon is practically not there.

- Q: Silicon is probably radiating in all directions ----?
- A: Oh, it is later on, at 500°C, at the point of operation. But if you keep the free-carrier absorption down, your silicon is still transparent and the emissivity is determined by the silver underneath.
- Q: Surely, at 500°C you have a lot of free-carriers and things that degenerate?
- A: It just starts after that. They could probably go up to 700°C or so. The free-carrier goes up steeply beyond. But at 500°C, I think the absorption coefficient, alpha, is on the order of three to five reciprocal centimeters. The band gap is sufficiently wide to keep the intrinsic generation down.
- Q: Do you have any estimate of the long-range cost of this film conglomeration?
- A: No, we haven't evaluated this yet. The process is ideal, of course, for large scale. You want to have pipes, which is very easy in the CVD area.
- Q: Have you attempted to compare photovoltaics to your system?
- A: No, we haven't done this.
- Q: This collector looks like it is more expensive than a solar cell to me.
- A: I couldn't judge this. We have simply never compared it to direct conversion.
- Q: Are you using CVD for the A-R coating? Have you actually done that?
- A: Yes, we have done this. In the last quarter we have developed the sequence of nitride, nitride-oxide and oxide, and in the future, hope to put the two together.
- Q: Can you control the thickness satisfactorily with the CVD deposits?
- A: Very well, yes. We do this by an in-process emittance control. This is also a way to check on the kind of material that we deposit.
- Q: What wavelength do you use?
- A: We have a two-micron interference filter and PbS cell.
- Q: How stable are these layers at 500°C? Do you get diffusion?
- A: No, that's the nice thing about the method. We make them at 650°C, so they behave well at 500°C. If you make them at room temperature, of course, you introduce a stress. We have Auger-spectra analyzed those layers (Prof. Wehner at the University of Minnesota has done it for us), and after 100 hours at 700°C, there was no interfacial diffusion or anything like that.
- Q: Are there any other materials you have considered as well as silicon?
- A: Yes. There are a variety of semiconductor compounds and mixed crystals and we have theoretically calculated the performance of other combinations and mixed crystals of germanium-silicon and so on. Anything qualifies that has a band gap approximately at the crossover point.
- Q: If you use a material that has a direct band gap instead of indirect, is it preferable?
- A: Yes. Silicon has a handicap, since it is an indirect-gap semiconductor.

**SESSION III**  
**SYSTEMS AND DIAGNOSTICS**

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### **SESSION III. SYSTEMS AND DIAGNOSTICS**

**MeV ION BACKSCATTERING—MICROSCOPY WITH MASS AND DEPTH PERCEPTION—M. A. Nicolet  
and J. W. Mayer**

**THE NSF FUNDED DIAGNOSTIC LABORATORY AT LBL—W. J. Siekhaus**

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## MeV ION BACKSCATTERING – MICROSCOPY WITH MASS AND DEPTH PERCEPTION

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### Presentation Summary

#### Principles of Backscattering Spectrometry

A monoenergetic beam of  $\text{He}^+$  or  $\text{H}^+$  ions in the MeV range penetrates into a solid target to depths ranging from several thousand  $\text{\AA}$  for targets composed of heavy atoms, to several  $\mu\text{m}$  for targets composed of light elements. A few of the penetrating particles undergo large-angle (Rutherford) scattering by direct collision with nuclei of the target atoms. The energy of the impinging ion after the collision is less than that the ion had immediately before the collision, and by an amount which depends only on the mass ratio of incident ion to target atom, and on the scattering angle (simple two-body collision). The energy of a backscattered particle thus characterizes the mass of target atom. By performing an energy analysis of the backscattered particles, one can deduce the mass of the atoms present in the target. Typical mass resolutions achieved are  $\pm 1$  atomic mass unit for light elements (up to Cl), and  $\pm 10$  mass units for very heavy atoms. Figure 1 (top) gives schematically the spectrum one would observe for backscattering from an equal number of Au and Al atoms deposited on the surface of a light substrate (whose backscattering signal is not shown in the spectrum). The Au atoms produce much larger yields because the cross section for Rutherford scattering increases as the square of the atomic number  $Z$  of the scattering atom. Backscattering spectrometry is thus very much more sensitive to heavy masses than to light ones. The cross sections are very well known, so that yield ratios of backscattering spectra can be translated into relative atomic ratios with good accuracy ( $\pm 5\%$ ).

As the beam penetrates the target, the ions lose energy. A collision with an atom inside the target generates a backscattered particle whose energy is less than that which would have been observed for a collision with the same atom at the surface. The energy shift is proportional to the amount of mass traversed by the particle. A uniform film of finite thickness thus generates an energy spectrum of backscattered particles which covers a finite range of energies. This energy range is proportional to the thickness of the film as long as its magnitude is small relative to the initial energy. Figure 1 (center) shows how energy loss generates depth perception in a backscattering spectrum. A typical depth resolution is about  $200\text{\AA}$ .

A backscattering spectrum provides the distribution of various atoms in depth over thousands of  $\text{\AA}$ , and the relative ratios of the atoms. The composition of these atoms in chemical compounds cannot be ascertained from such spectra. X-ray diffraction is a technique which can provide this information and complements backscattering well. The ion beam has a typical cross section of  $1\text{ mm}^2$ . Backscattering spectroscopy thus does not possess lateral microscopic resolution. Scanning electron microscopes are very helpful in assessing the lateral uniformity of the samples analyzed by backscattering. Details on backscattering spectrometry and its applications are found in recent reviews (Refs. 1, 2).

#### Some Applications to Thin Films

Thin deposited films tend to react with each other or with the substrate more rapidly than their bulk counterparts. A schematic spectrum indicating the formation of  $\text{AuAl}_2$  at  $200^\circ\text{C}$  is given at the bottom of Fig. 1 (Ref. 3). Reactions at low temperatures have been observed for many transition metal with Si (Ref. 4) or  $\text{SiO}_2$  (Ref. 5) substrates, and with air (Refs. 6, 7).

Figure 2 (top) shows a backscattering spectrum of a multi-layer optical coating consisting of 670Å ZnS and 1056Å ThF<sub>4</sub> layers. The effective resolution can be improved by tilting the sample against the beam (bottom). The sharp edges in the signal of the first layer prove that the films are well defined. The decreasing sharpness of the signals from lower-lying layers is due to the energy straggling of the incident beam. Figure 3 is a spectrum taken on a CdS/Cu<sub>2</sub>S sample. The sharp Cu edge shows that Cu is indeed present at the surface, but the poorly defined edge of Cd also reveals that a good definition of layers is not maintained in depth. The spectrum as a whole strongly suggests a highly non-uniform target. A clear-cut interpretation of this spectrum is possible only with additional information on the sample.

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### Discussion

- Q: On the migration experiments at 275°C that you showed, did you do those in such a way as to insure that the energy of the beam itself was not promoting the migration?
- A: These spectra were taken after the sample was annealed and cooled, walked to the analyzer, and mounted. We are also seeing effects due to the beam itself, but not in metals; not in these systems. We have analyzed just about anything you can think of including freeze-dried beef to look for lead, but that doesn't work very well.
- Q: You have indicated that if there is an interdiffusion layer; you can see it in your spectrum. Suppose you had an interface that was not smooth, but rather was sinusoidal. Would that not show up the same way in your spectrum?
- A: If the layer on top of your sinusoidally formed substrate has very much the same thickness, the effect is of small significance. If, on the other hand, your top layer is flat and the wiggles are on the bottom, then of course you have a major effect. That's what I said, we need scanning electron microscope pictures to assure that our interpretation is right.
- Q: What was the lateral resolution of this instrument?
- A: One millimeter. That's a spot size. You can move over to another spot and we can tell you whether that's the same thing as before. But we still do not have lateral resolution in microscopic terms.
- Q: There seems to be a rise in the yield as you go in. Is that because of energy loss in the direct beam? Or an increase in cross section?
- A: Yes. The former. There are additional effects besides that. But, basically, it's that.

**Q:** How does this compare with the electron probe, where you look at the X-ray spectra from electrons?

**A:** An electron probe typically has good lateral resolution, as good as your electron spot may be, but it has poor depth resolution. It excites a whole range of depth and you cannot determine whether the X-rays come from deep in or from farther up. The electron probe is a very useful complement, but it does have the much reduced depth perception along with the better lateral resolution.

**Q:** Could you give me a feeling for the absolute sensitivity of this? Let me give you a comparison – for a mass spectrograph, you have to have about  $10^{11}$  atoms in order to get a signal. What's the absolute sensitivity of this technique?

**A:** That's a hard question to answer. I am not trying to be evasive, but it is the nature of that tool. Practically we can say that a tenth of a monolayer of gold on top of silicon is measurable.

Backscattering — Depth Microscopy

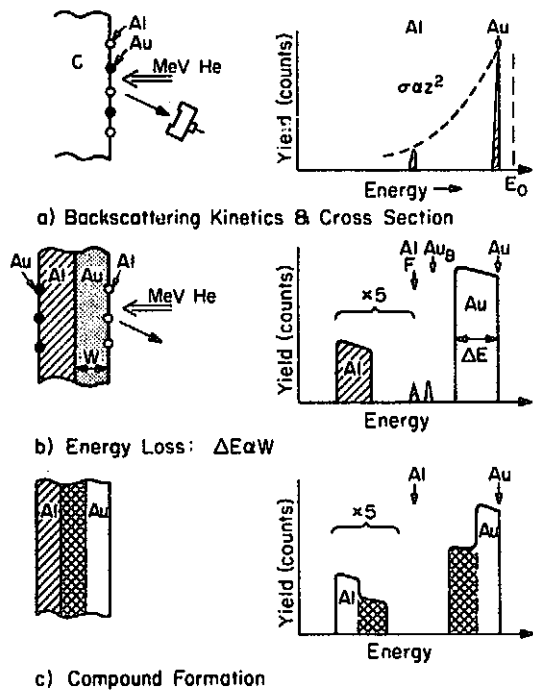


Fig. 1. (Top) Left: Principle of the layout; Right: Signals generated by equal numbers of Al and Au atoms on surface of a light substrate. To each mass of the target corresponds a particular energy below  $E_0$ . (Center): Layers of finite thickness generate signals of finite energy width, related linearly to each other; the upper film (Au) acts as an energy absorber which shifts the signal of the lower film (Al) towards lower energies. (Bottom): A reaction at the interface of two films is revealed by corresponding changes in the backscattering spectrum (compare with center part of the figure).

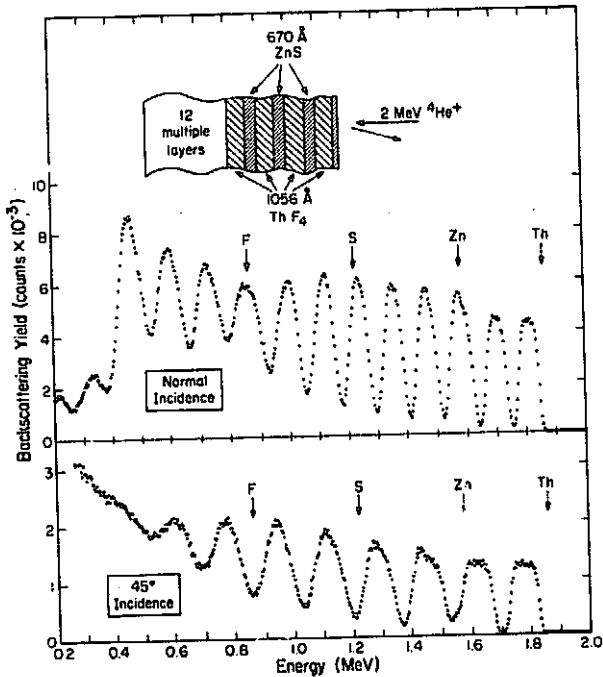
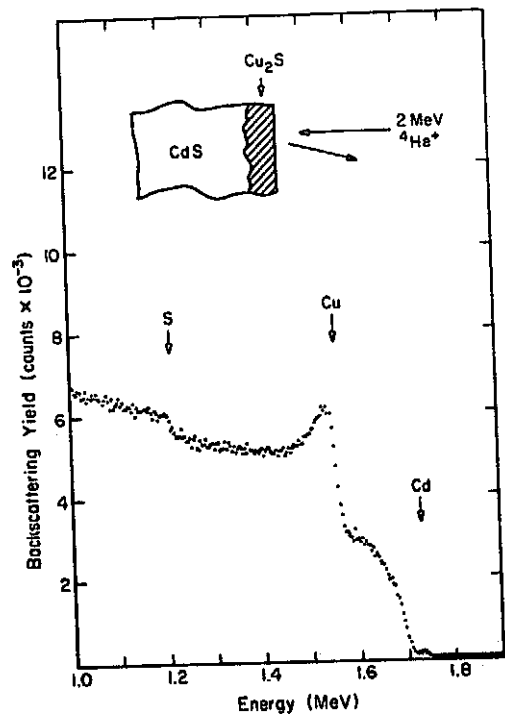


Fig. 2. The backscattering spectrum of a twelve-layer optical coating obtained with 2.0 MeV  $^4\text{He}^+$  at normal incidence of the beam. The decrease in resolution with depth is due to energy straggling of the incident beam. When the target is tilted against the incident beam, the effective thickness of the layers increases, resulting in a corresponding effective increase in resolution (from Ref. 4).

Fig. 3. Backscattering spectrum of CdS/Cu<sub>2</sub>S samples, obtained with 2.0 MeV  $^4\text{He}^+$  at normal incidence. Cu and S appear to be present at the surface (sharp edges), but the remaining features of the spectrum strongly suggest a very nonuniform target.



## THE NSF FUNDED DIAGNOSTIC LABORATORY AT LBL

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### Presentation Summary

The surface chemistry and surface physics laboratory under Professor Somorjai at the Lawrence Berkeley Laboratory in Berkeley, of which the photovoltaic diagnostics group is a part, has worked for about 10 years on problems of surface structure determination by low energy electron diffraction, on the specificity of surface structures and surface constituents for catalytic chemical reactions using Auger spectroscopy, mass spectroscopy and modulated molecular beam spectroscopy, and on problems related to the preferred surface segregation of constituents of certain alloys. We believe that the expertise we have in the field of surface physics and surface chemistry and the instrumentation which we have dedicated to photovoltaics can help to identify and to solve surface and interface problems which limit the efficiency and life of photovoltaic devices.

Let me demonstrate, using the example of a possible polycrystalline thin film cell, the problem areas of interest (Fig. 1). We have a surface, or an interface which once was a surface during the course of the cell production, at positions a, b, b' and c. At each of these interfaces two questions have to be answered: (1) which materials are present and in which chemical form (either intentionally or unintentionally) from an unknown source during production and (2) how do these materials affect the life and performance of the photovoltaic device. We have dedicated one instrument (a scanning Auger microscope with ion etching equipment) to the first question. It will become operational at the beginning of the next year. A high-resolution electron spectrometer intended to measure surface states is dedicated to the second question. It will become operational at the beginning of the next month.

These are the problems to be expected at the interfaces:

- (a) If this is a thin film deposited on the substrate, impurities and natural constituents are likely to diffuse at the deposition temperature through the bulk and certainly along the interfaces. Materials and processes should be chosen to minimize the impact of this effect. Pichaud and Drechsler (Ref. 1) have shown that the presence of some impurities increases the self-diffusion of atoms and hence the likelihood that a crystalline layer can be deposited.
- (b) The identification of impurities at grain boundaries may well show why the crystal growth process was stopped and a new grain begun.
- (b') It is unlikely that in a thin-film cell all grain boundaries can be eliminated, and certainly all surfaces cannot be eliminated. But the complete review by Mönch (Ref. 2) and more recent work by Rowe and Ibach (Ref. 3) show clearly that the detrimental effects of surfaces—their large concentration of surface states which lead to fast and slow surface traps—can be alleviated, decreased by orders of magnitude by exposure treatment with some gases. This effect will be systematically investigated on various crystallographic surfaces using our high resolution spectrometer. That desirable interfaces can be created by proper treatment has been demonstrated convincingly by Martinelli (Ref. 4) who reported "negative electron affinity" for some surfaces covered suitably with cesium and oxygen.
- (c) A contact that comes off during tape testing or during exposure to environmental lifetests has most likely suffered a catastrophic exposure to some gas or impurity during production. Auger analysis would reveal the source of the problem.

There is one more area where the diagnostic and analysis laboratory being setup will be employed: the investigation of the catalytic mechanism that lowers the silicon deposition temperature in the presence of diborane by several hundred degrees (Ref. 5). The understanding of this mechanism may lead to substantial decreases in the deposition cost of polycrystalline silicon.

Let me summarize and repeat, we will have shortly two instruments dedicated to analyzing structural, chemical and electronic properties of photovoltaic device surfaces.

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### Discussion

Q: In scanning Auger, what size is your beam?

A: The beam is physically an electronic system. So the beam size is approximately two microns, or less than two microns. That's all they specify. And in depth resolution, it is as good or as bad as any sputtering resolution - 20 to 200 angstroms, ten percent over the thickness of the film.

Q: You said you have ion etching capability in there?

A: Yes. Sputtering.

Q: How flat is the surface that is etched?

A: Flat with respect to the size of the beam? Yes. The beam size for ion etching is considerably larger than one micron.

Q: As you are proceeding down through the layers, you are meeting various kinds of materials, all with different sputtering rates. Are you really looking at what you think you are looking at?

A: This is a question in all sputtering. It is a problem, but there are many systems in which it is relatively well understood. It is not a big problem. There is always diffusion of constituents, in the regime of the penetration depth of the ion beam, but the depth of penetration of the ion beams at sputtering energies of 500 V to at most 1 kV is maybe 20 angstroms. Resolution is never better than that. But as long as you keep to a relatively low sputtering rate, so that your energy deposition is not high enough to create long diffusion, your resolution will be that good.

Q: Do you think you could delineate diffusion profiles with these tools?

A: I said the sensitivity is one percent of a monolayer. That's pessimistic. Optimistically, a tenth of a percent of a monolayer would be better. So that's one part per thousand concentration in bulk. As long as your concentration that you want to look at is in that range, one certainly can. But I don't think that most doping concentrations are that high.



**Q:** What particular elements increase the deposition rate of silicon many times at low temperatures?

**A:** Diborane. There was an article on deposition of doped silicon material in the presence of diborane in the October issue of the *Journal of the Electrochemical Society*.

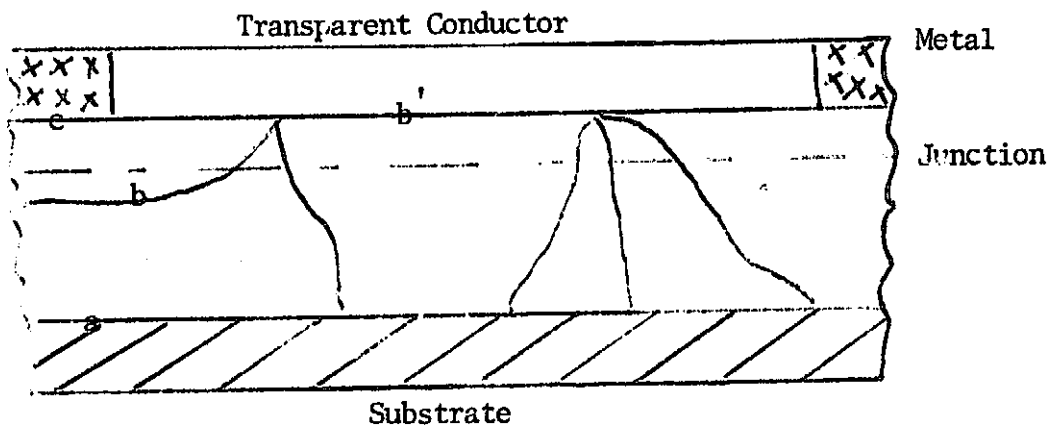


Fig. 1

## SELECTED AREA AND IN-DEPTH AUGER ANALYSIS OF THIN FILMS

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### Presentation Summary

Auger electron spectroscopy (AES) is based on the emission and subsequent energy analysis of secondary electrons produced by high-energy (3 to 5 keV) electron bombardment. The energy of a small fraction of the secondary electrons emitted from the sample can be related to the core levels of the target atom and these electrons, the Auger electrons, have escape depths in the 5 to 20 Å range. This low escape depth makes Auger electron spectroscopy ideal for surface analysis and for in-depth analysis when combined with *in situ* ion sputtering (Refs. 1, 2). AES has rapidly developed from a purely research oriented technique into an extremely versatile analytical method capable of localized (i.e., small selected volume) analysis on materials systems of technological importance.

This rapid growth began, perhaps, with the use of phase sensitive detection (Ref. 3) which was followed by the development (Ref. 4) and commercial availability of the cylindrical mirror analyzer (CMA). The CMA increased the applicability of the technique, since its increased S/N allowed for rapid data acquisition and oscilloscope display. Significant recent developments which have extended the analytical capabilities of Auger electron spectroscopy include:

- (1) In-depth analysis by combining Auger analysis with simultaneous *in situ* ion sputtering. Since sputtering is used to gradually erode the sample, depth resolution is dependent on factors such as surface topography, sample homogeneity, location of the primary electron beam in the crater formed by the primary sputtering ( $A^+$  or  $Xe^+$ ) ions and the mass and energy of the sputtering ion. For the case of optically flat and homogeneous samples, depth resolution is in the range of 5 to 10 percent of the sample thickness (Ref. 2) analyzed.

Preferential sputtering effects in alloys or compounds and the possibility of the induced mobilization of impurity ions, such as sodium in insulating samples, as a direct result of ion bombardment can complicate or prevent in-depth profile analysis by simultaneous Auger analysis and ion sputtering. The situation of gross preferential sputtering (Ref. 5) or induced mobilization (Ref. 6) is not typical, but can occur.

- (2) Selected area surface and in-depth analysis is possible by the use of an optical microscope (Ref. 7), video monitor with TV display (Ref. 7) or by scanning the primary electron beam to obtain sample current and secondary electron images (Ref. 8). Selected area analysis with high image resolution has also been obtained by incorporating Auger spectrometers into scanning electron microscopes (Ref. 9).

Selected area analysis makes the Auger technique suitable for the surface and in-depth analysis of specified thin film circuit components on a substrate such as resistors, capacitors, conductors, and bonding pads. The specified area analyzed is at present limited by electron beam spot size which is on the order of 25 to 100  $\mu\text{m}$ .

- (3) Quantitative analysis, while not completely developed, is possible via calibration with homogeneous standards of known composition (Refs. 10, 11). The calibration of Auger measurements for quantitative analysis has become possible with the development of simultaneous *in situ* ion sputtering-Augur analysis.

The above capabilities make the Auger technique ideally suited for thin film materials characterization. This paper will describe: (1) quantitative analysis of light elements (N, C, O) in sputtered tantalum films by Auger electron spectroscopy via calibration with standards, and (2) selected area surface and in-depth analysis on thin film systems.

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### Discussion

(Not recorded.)

## TECHNIQUES FOR THE DETERMINATION OF THE PHASES IN THE SURFACE LAYERS OF CdS/Cu<sub>2</sub>S CELLS

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### Presentation Summary

This report is concerned with work in progress in which a combination of methods is being used to determine the reaction products in the near surface layers of the cadmium sulfide cell (Ref. 1). The discussion describes the employment of scanning electron microscopy, Auger spectrography, transmission electron microscopy and selected area diffraction. Recent research (Ref. 2) has indicated that the quality of copper sulfide-cadmium sulfide solar cells is greatly dependent upon the phases present in the surface layers. An increasing amount of digenite was associated with a reduction of the short-circuit current, and it was concluded that chalcocite is important for good yield cells. Alternate methods of studying the above conclusions are necessary.

### Scanning Electron Microscopy

Consider the schematic cross section of a CdS/Cu<sub>2</sub>S cell as illustrated in Fig. 1. This Cleveite-type cell is composed of a copper substrate with a surface-alloyed zinc layer. On this layer is a vapor-deposited, etched, polycrystalline film of CdS. The barrier shown is believed to follow the surfaces and the grain boundaries. A simple method by which the cross section and details of the topography of the various components of the cell can be observed is based on fracturing the brittle CdS and viewing the resulting structure by scanning electron microscopy (Ref. 3). Examples are shown in Fig. 2. The important regions are indicated as follows: A, zinc-coated substrate; B, surface of the reacted cadmium-sulfide layer; and C, the fracture-surface cross section. This method of producing a cross section can separate the cadmium sulfide from the substrate as shown at D. In Fig. 2b, columnar-type grains, whose boundaries diverge from nucleation sites at the substrate, are seen. The thin reaction layer of copper sulfide is not made visible by this technique. However, if the thin copper sulfide layer is magnified by producing a tapered cross section by ion sputtering as illustrated in Fig. 3, and a reversed bias is established in the cell, the difference in potential between the p- and n-type regions result in a voltage contrast (Ref. 4) when viewed in the scanning electron microscope. It is therefore possible to control the contrast by varying the voltage difference. This effect is shown in Fig. 4: the dark region, T, is the copper sulfide layer; the corrugated appearance of the tapered cross-section is a result of ion-beam milling in one direction. Although this method gives some indication of the thickness of the layer, it cannot specify the phases present.

### Electron Diffraction of Thin Layers

Let us now consider an electron diffraction study of the reaction layer. In these experiments both single and polycrystalline specimens of CdS were thinned to electron transparency by ion milling. Selected area diffraction patterns were taken at different orientations. For polycrystalline specimens, large grains were selected for study. Figure 5a is a diffraction pattern of a thinned single crystal of CdS. This is a pattern of cadmium sulfide oriented with the b direction perpendicular to the plane of viewing. Symmetrical Kikuchi lines indicate the accuracy of this orientation. This specimen was then removed from the electron microscope and treated with a cuprous chloride solution, washed, and returned to the electron microscope. The new diffraction pattern in Fig. 5b is composed of CdS, but in addition, a new pattern has developed. The original CdS pattern is indicated by the dotted rectangle. From the symmetry and arrangement of diffraction spots, the new pattern is identified as Cu<sub>2</sub>S. For the same orientation, reciprocal lattice points of Cu<sub>2</sub>S are superimposed on those of CdS in Figure 6a; the spacings are based

on the values reported in the literature (Ref. 5). Note that the reciprocal lattice points from similarly spaced planes do not coincide ( $211\bar{2}$  of CdS and  $60\bar{4}$  of  $\text{Cu}_2\text{S}$ , for example). The insert in the diffraction pattern, Fig. 5a, shows the manifestation of this difference in separation.

In Fig. 7a, a diffraction pattern oriented with the b direction  $10.5^\circ$  from the normal to the electron beam is shown. After dipping in cuprous chloride, triplet diffraction spots are evident as seen in Fig. 7b. If reciprocal lattice points from CdS,  $\text{Cu}_2\text{S}$  and  $\text{Cu}_{1.96}\text{S}$  are combined (superimpose Fig. 6a and Fig. 6b), the triplet spots can be accounted for. For example, see the insert at the bottom of Fig. 7b in which  $1\bar{1}3_c$  (chalcocite) and  $1\bar{1}3_d$  (djurleite) are identified. Thus, for the treatment given these specimens, chalcocite, cadmium sulfide and djurleite (Ref. 6) are present.

Since cadmium sulfide and chalcocite are epitaxial layers and the spacing between planes are slightly different, Moire fringes (Ref. 7) can be produced in transmission electron microscopy by forming an image with two nearby diffraction spots such as  $2\bar{1}\bar{1}0$  (CdS) and  $600$  ( $\text{Cu}_2\text{S}$ ). From the lattice parameters available, the Moire fringe distance is calculated to be  $44\text{\AA}$ . In Fig. 8, the fringe distance is measured to be  $56\text{\AA}$ , an experimental value which is reasonably close to the calculated values.

#### Auger Spectrography

Auger spectrography is employed to determine elements on surfaces of solids. When dipped cells were analyzed, significant amounts of oxygen, carbon, chlorine and cadmium, in addition to sulfur and copper, were found (see Figure 9a). The oxygen and carbon are usually atmospheric in origin; whereas, the chlorine and cadmium must come from the dipping solution. (Note in Fig. 8, the cube artifacts are probably NaCl that were not removed by washing.) If ion sputtering is used to remove surface layers in conjunction with the collection and detection of Auger electrons, a compositional profile as a function of depth can be established. With the instrument in our laboratory, the two processes are accomplished simultaneously, the Auger peaks of specific elements are continuously recorded. Typical results are shown in Fig. 9b. Quantitative information from Auger analysis is difficult to obtain since standards are necessary. At present, standards for  $\text{Cu}_2\text{S}$  and  $\text{Cu}_{1.96}\text{S}$  are being prepared in our laboratory.

In spite of the limitations on absolute concentration determinations, relative amounts of elements have been obtained and tentative identifications of the phases have been made for a number of films. Preliminary results suggest that the cells with good fill factors are composed of a layer of chalcocite that extends about halfway into the reaction layer. The remaining portion of the reaction layer appears to be djurleite. Poor cells which were tested apparently did not contain significant amounts of chalcocite.

The techniques demonstrated in this paper are useful for studying thin layers near the surface. Although the work is not complete, there is a strong indication that the question of whether a large amount of djurleite effects the electrical characteristics of the cells can be finally solved. The techniques are not time-consuming, although careful preparations are necessary. Still required for quantitative measurements are: (1) standards of chalcocite and djurleite for Auger spectroscopy; (2) an improved sputtering technique where even surfaces are produced; (3) an analysis of sputtering in which the buildup or the selectivity of the elements are clearly shown.

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**Discussion**

(Not recorded)

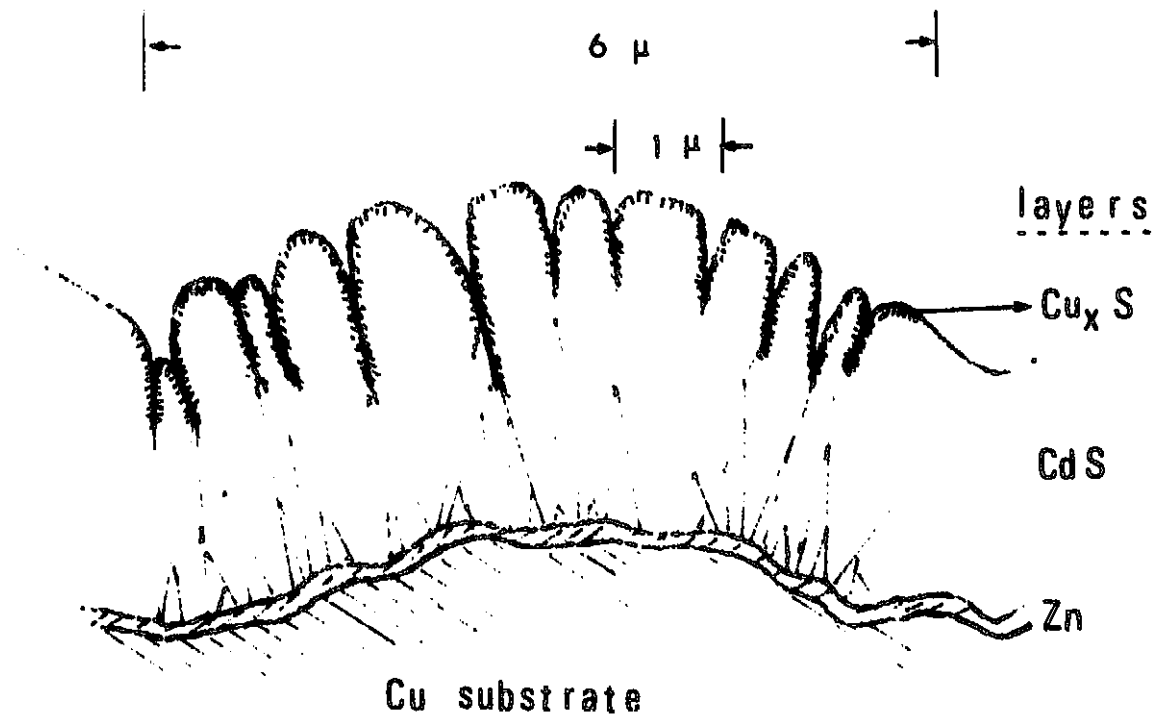


Fig. 1. Schematic Topograph of  $\text{Cu}_x\text{S}/\text{CdS}$  Cell



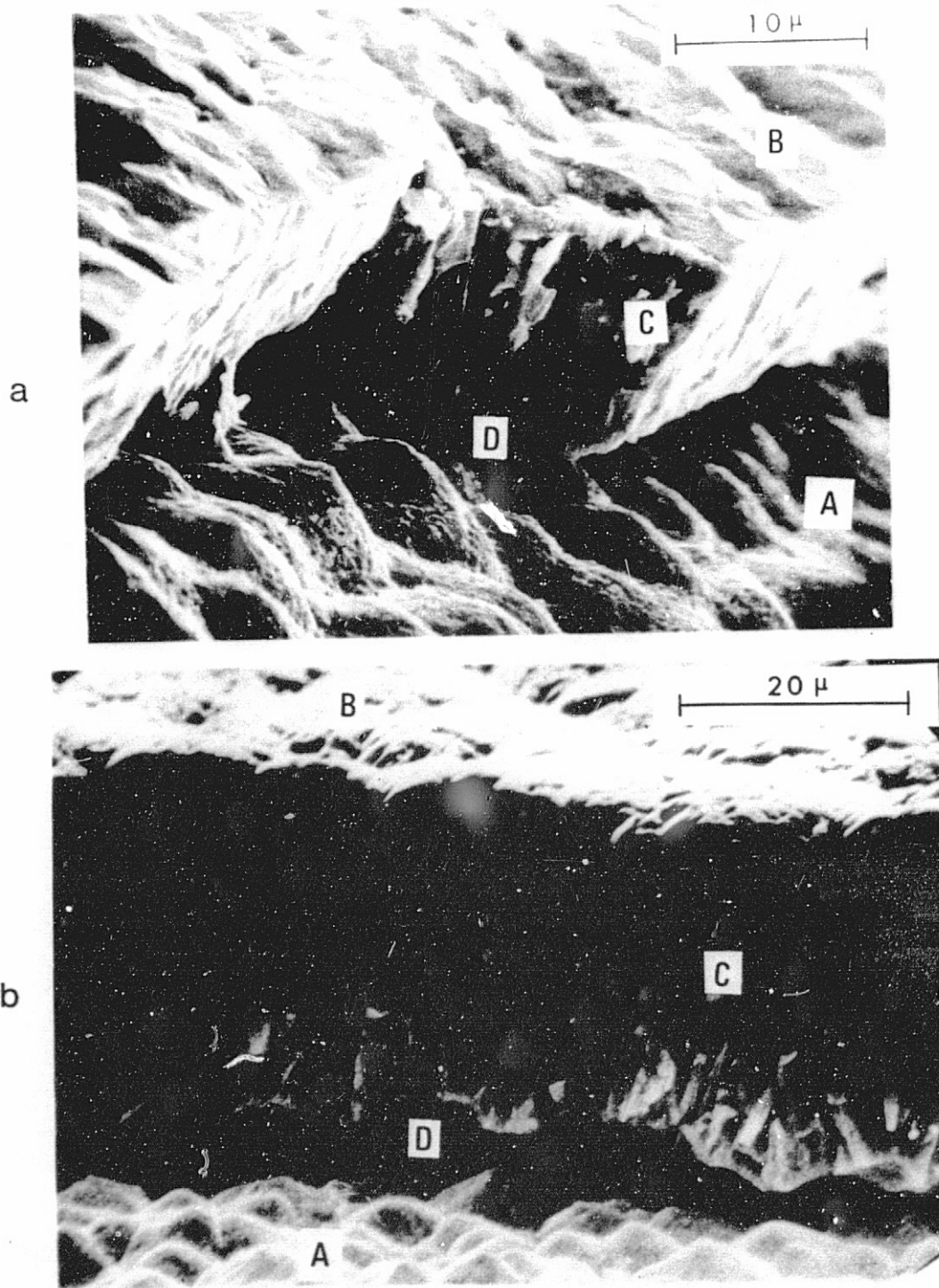


Fig. 2. Layer of Cadmium Sulfide on Zinc Coated Copper Substrate. Region A is the Zinc Casted Copper Substrate; B is the Surface of the Cadmium Sulfide; C is the Fracture of the Cadmium Sulfide

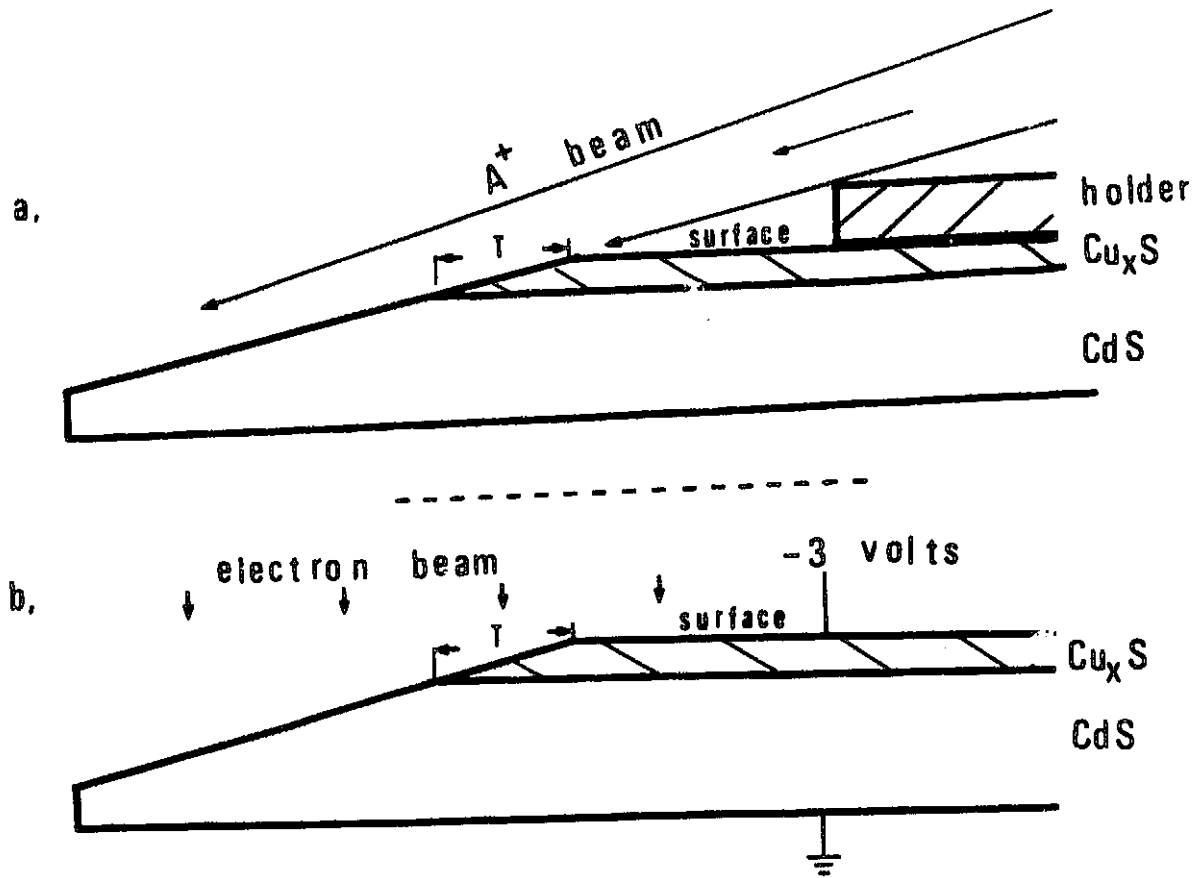


Fig. 3. (a) Tapered Cross-Section Produced by Ion Sputtering;  
(b) Position in Scanning Electron Microscope (Reverse Bias);  
T is the Tapered Cross-Section of Cu<sub>x</sub>S Layer

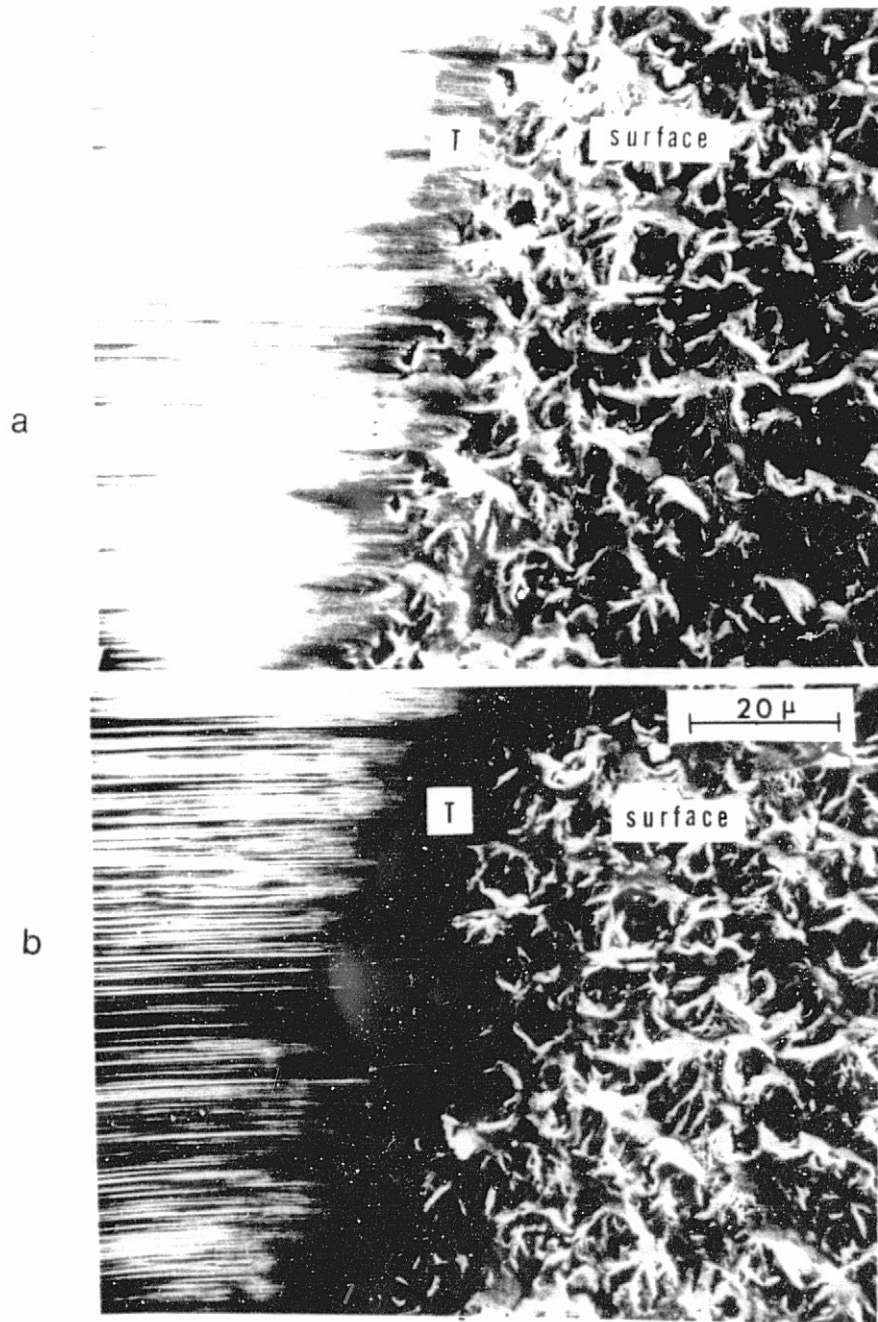


Fig. 4. Voltage Contrasts of  $\text{Cu}_x\text{S}$  (p-type)/CdS (n-type) Cell Reverse Biased (a) 0 Volts and (b) 3 Volts

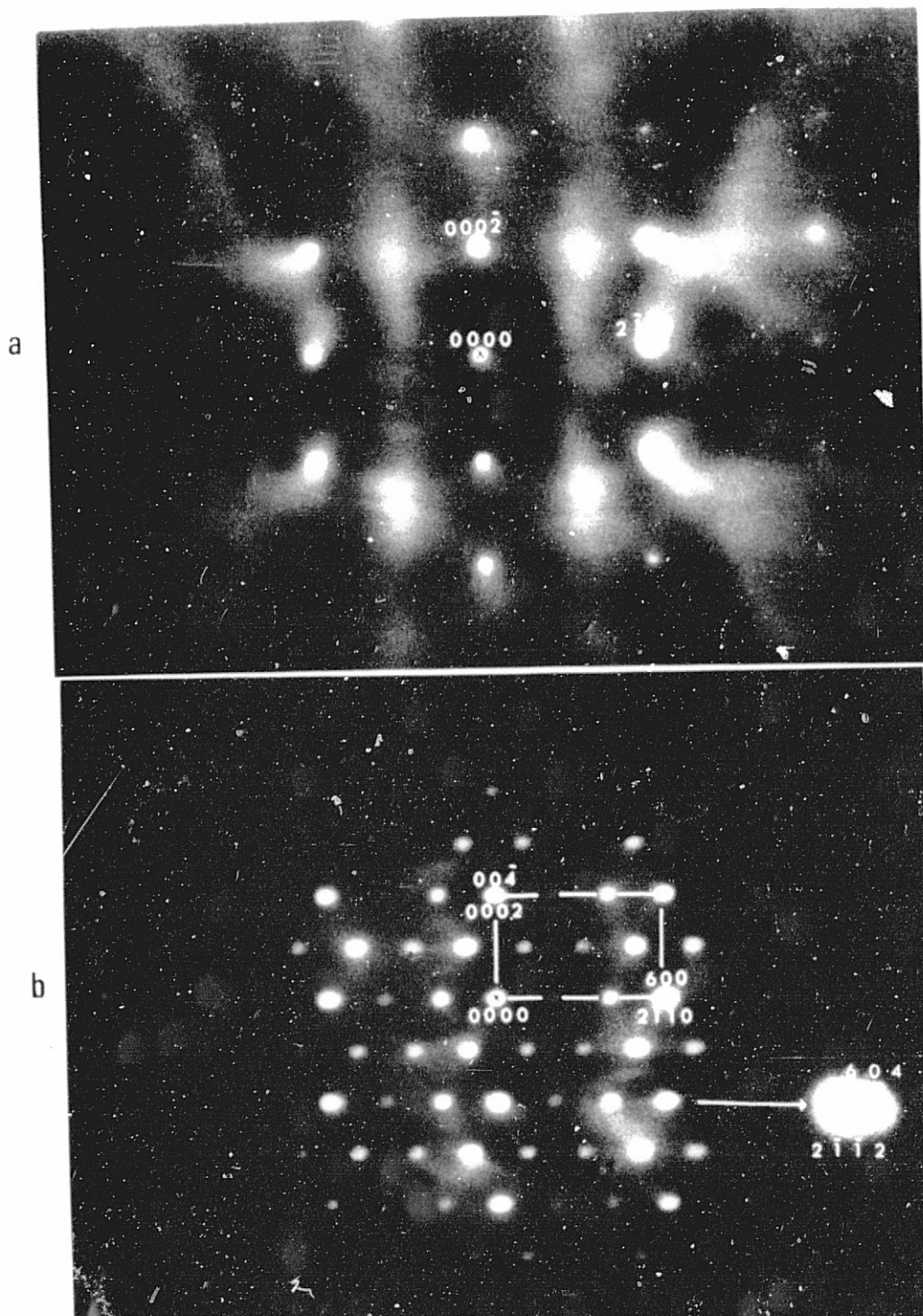


Fig. 5.  $[01\bar{1}0]$  Electron Diffraction Patterns of Cadmium Sulfide (a) Before and (b) After Converting Thin Layer of Cadmium Sulfide to Copper Substrate

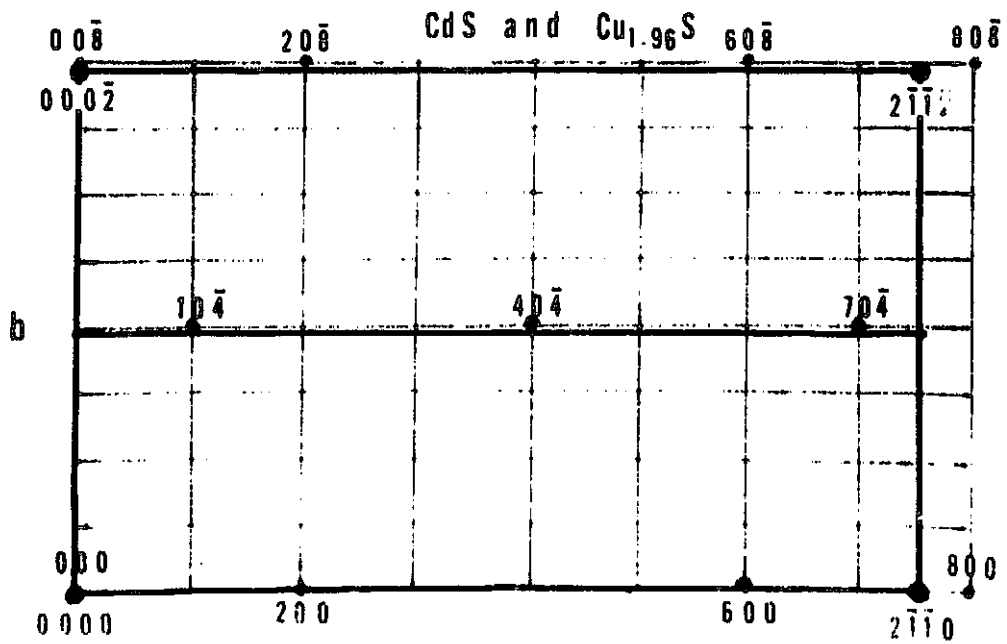
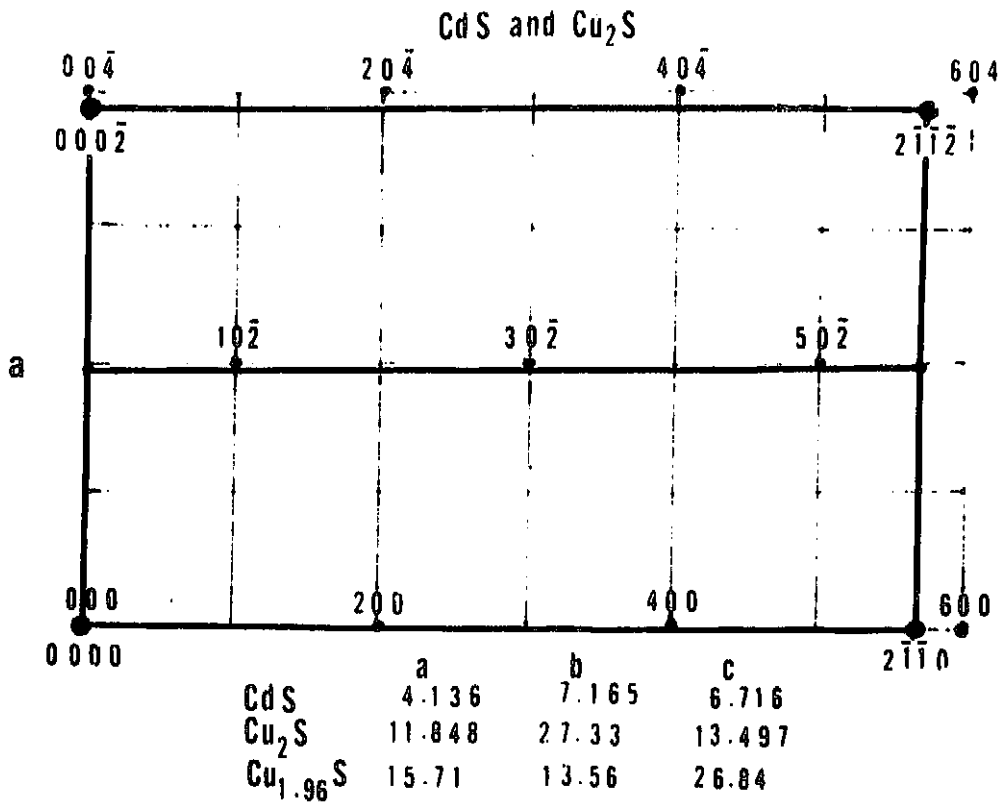


Fig. 6. (a) [010] and [010] Reciprocal Lattices of CdS and Cu<sub>2</sub>S  
 (b) [010] and [010] Reciprocal Lattices of CdS and Cu<sub>1.96</sub>S

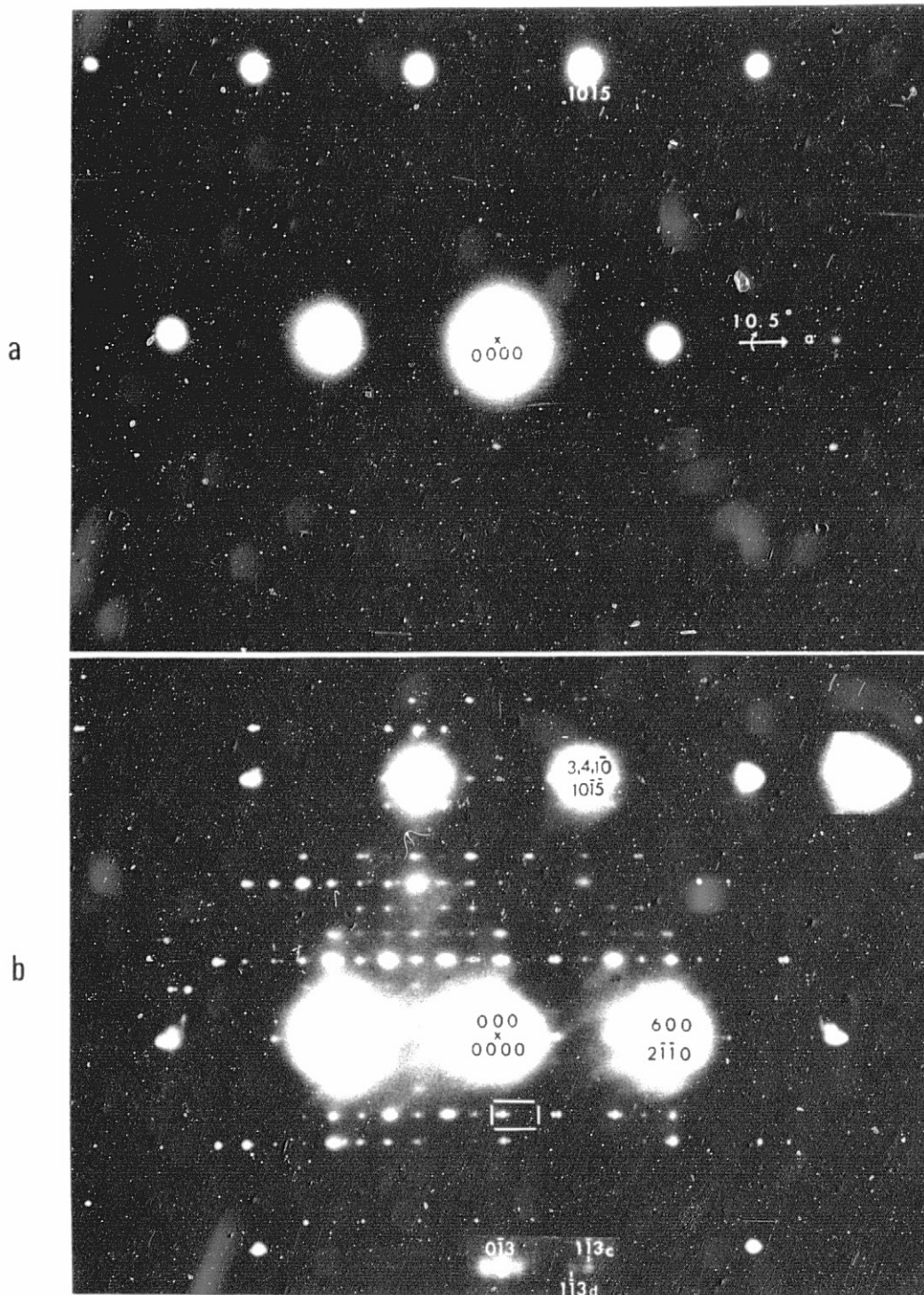


Fig. 7. (a) and (b) Tilting  $10.5^\circ$  About  $2\bar{1}\bar{1}0$  (or 100) Shown in Figure 5

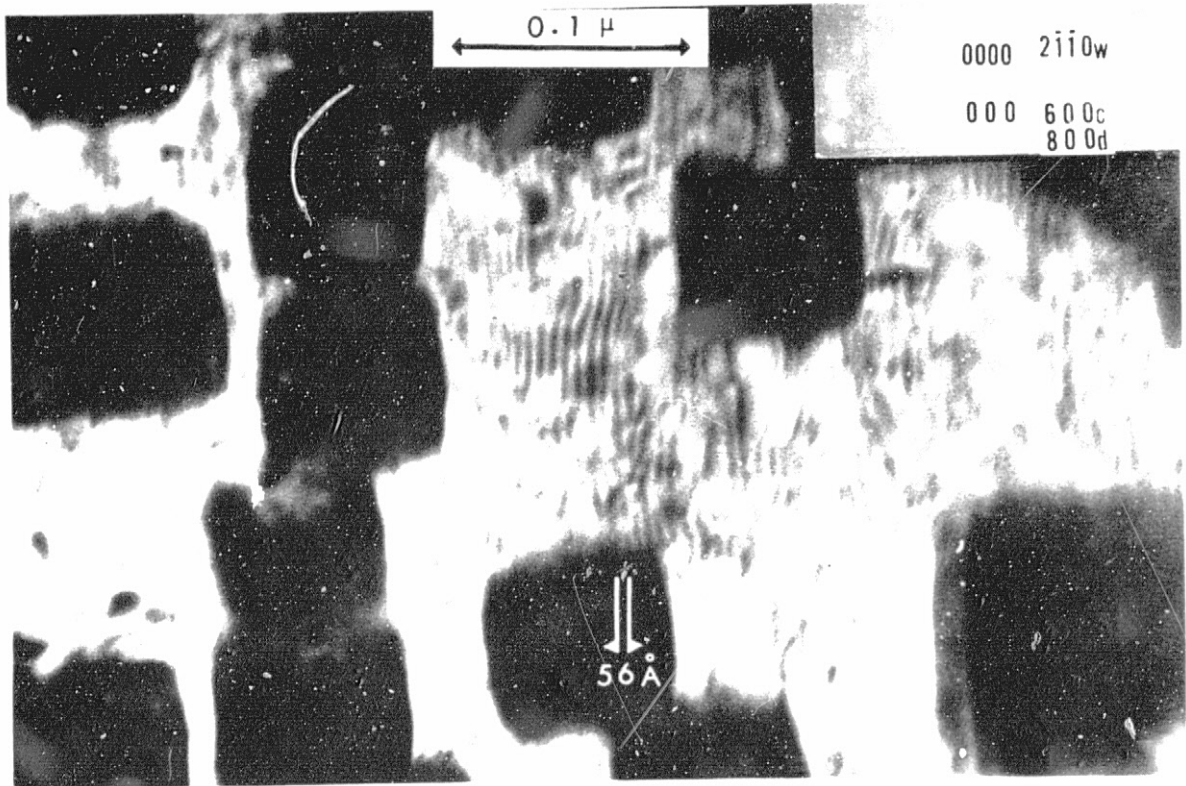


Fig. 8. Transmission Electron Micrograph Showing Moire Fringes in a Dipped Cadmium Sulfide

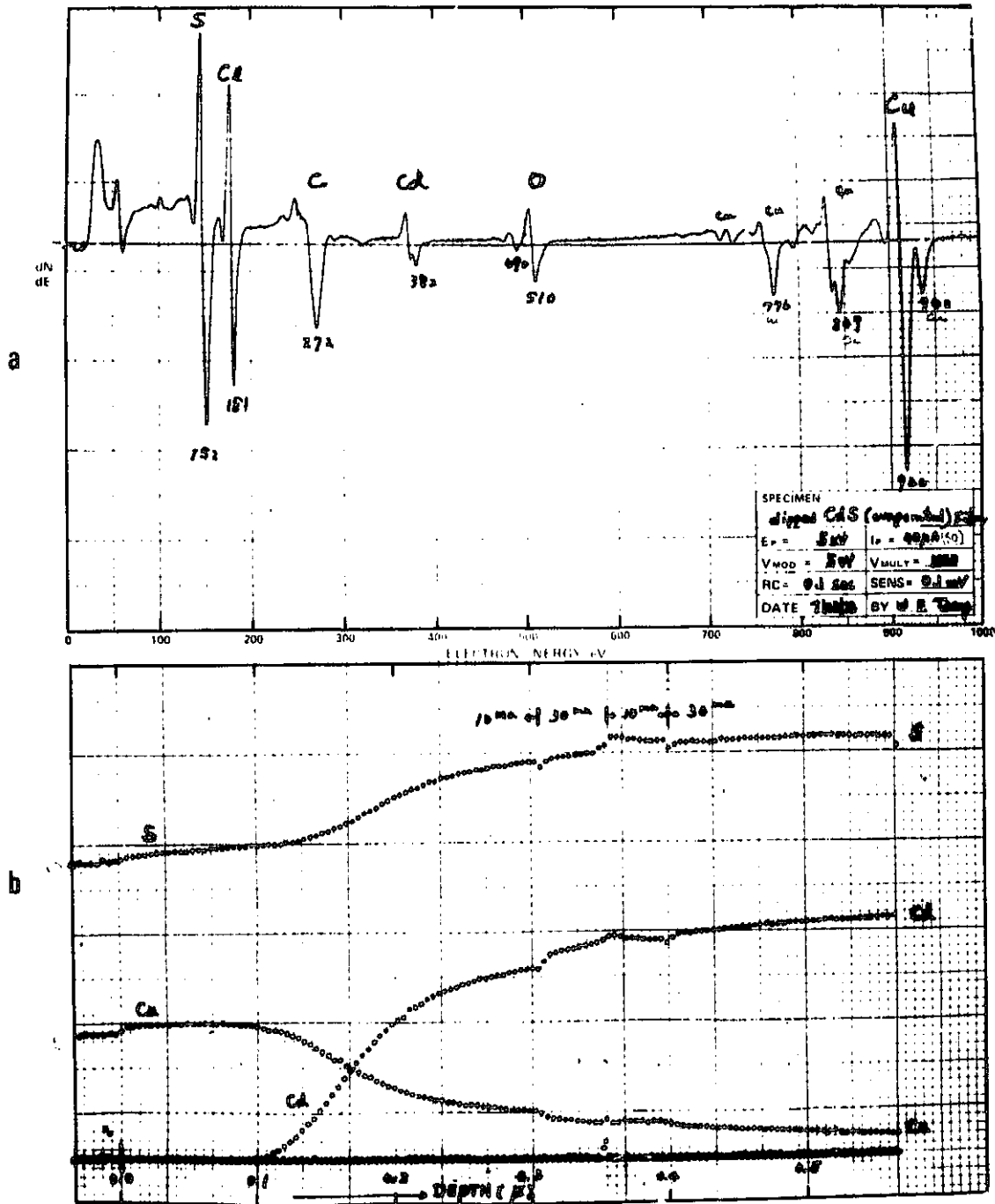


Fig. 9. (a) Typical Derivative Auger Electron Peaks Obtained from Surface Layer of a  $Cu_xS/CdS$  Cell (b) Curves of Derivative Auger Electron Peaks of Cu, S and Cd versus Distance from Surface of the Cell in (a)



## CONCENTRATION ONTO SOLAR CELLS

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### Presentation Summary

A joint program involving Arizona State University and The SpectroLab/Heliotek, Division of Textron, Inc., is just starting to investigate the degree of cost reduction achievable in photovoltaic power systems that are a result of applying solar concentration techniques. This effort complements the other NSF photovoltaic programs that are directed toward reducing the cost of making the solar cells.

It was shown in 1965 that silicon solar cells can be operated at solar concentration ratios of over 300 to 1 and still exhibit efficiencies of about 5% (Ref. 1). Since the device is able to produce well over one hundred times the amount of power as it could without concentration, the cost of the power associated with the device becomes about 100 times smaller when compared on a dollar per watt basis. This provides a significant cost reduction tool with which to work. There must be a tradeoff made to determine the largest advantage obtainable as one replaces the relatively expensive solar cell with a less expensive solar concentration system. As the concentration ratio increases the complexity of the cell, the heat transfer unit, the concentrator design and the orientation system increases. The primary objective of this program is to analyze the parameters applicable to this tradeoff and to optimize to the lowest cost to watt ratio. The economic goals of the program are to show that photovoltaic systems can reach the competitive cost range of 50 cents to \$1 per peak watt without requiring any "breakthroughs" in the making of solar cells.

A large range of concentration ratios (1 to 1000) will be investigated. The high concentration ratios are of interest for use with present cost cells but the lower ratios are also of interest for coupling with lower cost cells that may be developed through other programs. It is very likely that a combination of a lower cost cell with some degree of concentration will be the first competitive large-scale photovoltaic system. This study should provide the parametric data on the various components upon which an economical system could be designed.

Heliotek will be primarily concerned with determining the photovoltaic device performance characteristic as a function of the light level and solar cell temperature. Since the cell must be designed differently for different ranges of light intensities, an analysis of the device parameters that affect this performance will be made. The analysis will show how the performance is affected by grid design, cell resistivity, semiconductor material (i.e., Si or GaAs), junction depth, junction configuration (i.e., planar or vertical multijunctions), cell size and thickness, contact method, antireflection coating, light spectrum, etc. As the sunlight intensity increases new optimum cell designs and performance characteristics will be determined. The analysis will provide sufficient data for determination of optimum cell design parameters for all sunlight levels that are likely to be obtained in the concentration system. Experimental verification of the analytical study will be obtained by fabricating solar cells and testing them in simulated light conditions. The temperature dependence of these cells will be determined. The solar cell mounting and interconnecting design will be analyzed to minimize thermal and mechanical stresses.

The device cooling techniques will be investigated by ASU with close cooperation with Heliotek on the device mounting requirements. A complete range of possible heat-transfer techniques, both active and passive, will be analyzed and their appropriateness for accommodating various ranges of concentration ratios will be identified.

The techniques to be considered will include free convection, radiation, heat pipes, natural-circulation, single-phase forced convection, nucleate boiling, two-phase thermosyphons, and various combinations of these techniques. Several cooling fluids will be considered with compatibility with the mechanical and electrical properties of cells

taken into account. All of the device cooling will be done while taking full cognizance of the possible system configurations in which the cooling technique will be used. The ultimate heat rejected from the system is primarily considered to be dissipation to the atmosphere although the alternative of utilizing this energy is possible.

Besides the normal considerations for concentrators such as cost, accuracy, efficiency and concentration ratios there will be further evaluations of cleaning techniques, compatibility with the cell heat rejection system, and life-time in atmospheric conditions.

It is expected that the program herein described would take about 18 months. Recommendations will then be made for a prototype system design (or designs) that represent attractive cost reductions, which can be built and tested in a follow-on effort.

#### Reference

1. Schoffer, P. and W. Beckman, "Photovoltaic Power Systems Using High Solar Energy Fluxes," Final Report to U.S. Army on Contract No. DA-28-043, University of Wisconsin, Engr. Exp. Station, Madison, Wisconsin, Dec. 1965.

#### Discussion

(Not recorded)

## A LOOK AT SOLAR POWER FOR SEATTLE -- REVISITED

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### Presentation Discussion

From 1972 to 1973 the Boeing Aerospace Company was engaged by Seattle City Light Co. to evaluate solar heat energy as a source of public utility type of power. A paper presented at the 1973 Intersociety Energy Conversion Engineering Conference (IECEC) discussed some of the problems we found associated with the conversion of solar thermal energy to electrical power (Ref. 1). Today's presentation will deal with providing solar power under the same ground rules but with photovoltaic energy conversion.

### Solar Plant Site Considerations

One of the tasks of the original study was to evaluate potential sites for a solar plant. The sites selected are also good for photovoltaic energy conversion. A major problem in site selection was a lack of insolation data and the questioned accuracy of available data. The Weather Bureau reports that the pyranometers used to measure solar insolation have degraded in performance, with the greatest degradation occurring in the sun-rich areas of the United States. Furthermore, the instruments for determining the amount of sunshine are subjectively set with respect to threshold, thus allowing for considerable error in defining what constitutes usable sunlight. There is thus a need to gather sufficient, accurate data for system analyses.

### Basic System Concept

The basic concept of a photovoltaic power plant is shown in Fig. 1, and the comparable solar thermal plant is shown in Fig. 2. The photovoltaic plant is much simpler, not requiring heat transport, mechanical machinery, or cooling.

### Problem Areas

Table 1 shows some of the problem areas. Heat transport is a major problem with the thermal plant. To obtain practical plant efficiencies it is necessary to run the energy converter at high temperature. For a Brayton cycle the heat must be transported with fluids at 875 to 925°C. These temperatures are at the upper limit of available pipe materials which are fifteen times the cost of steel. Insulation requires considerable development and cost, there never having been a need for transporting 900°C fluids for distances up to 500 feet.

Low-temperature (540°C) systems using the conventional Rankine cycle turbines may require the use of NaK, a liquid metal, to minimize pumping losses and avoid freezing at night. NaK is objectionable to many because of cost and safety. Photovoltaic conversion, of course, does not require heat transport.

Heat-reflecting concentrators require accurate orientation as they use only the specular component of sunlight. The solar cell converts both direct and diffuse components of the sunlight to electric power and thus does not need to be precisely orientated -- a ten percent error in orientation, which is disastrous for a concentrator, drops solar cell output by only 1.5 percent.

The variation in solar intensity on a short-time scale (minutes, hours) seriously impacts the design and operation of a solar thermal power plant. This relates back to the lack of good solar insolation data. Detailed data are required before a thermal plant can be properly optimized for a location. Loss of heat for any significant time can seriously affect plant operation and efficiency.

Solar collectors of high quality are hard to build. To achieve high concentration ratios (and high temperatures) requires an accurate, highly reflective surface which is costly. One sandstorm of the type that are common in

desert areas can completely ruin an unprotected reflecting surface. Our study for Seattle City Light Co. concluded that the solar concentrator is one of the costliest items in the system, and risky development of mass-produced concentrators is essential to bringing the cost of solar power to even within order of magnitude of the cost of nuclear power today.

The problems in photovoltaic conversion are the cost and efficiency of the solar arrays, which are already well documented. Cost reduction is, of course, essential to economic viability.

Both the photovoltaic and thermal system design is limited by the poor and/or inadequate solar insolation data. Likewise, both systems require costly storage systems if it is desired to have operational capability in sunless hours.

**Reference**

1. H. Oman and C. J. Bishop, Proceedings of the Intersociety Energy Conversion Engineering Conference, Philadelphia, Pa., August 1973.

**Discussion**

(Not recorded)

Table 1. Problem Areas of Solar Power Systems

Thermal	Photovoltaic	Both
Heat transport	Cost	Solar insolation data
Orientation	Efficiency	Energy storage
Radiation variation		
Solar collectors		
Quality		
Cost		

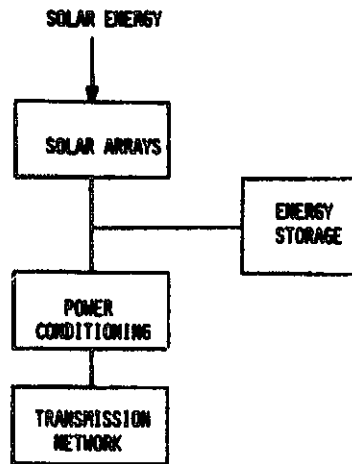


Fig. 1

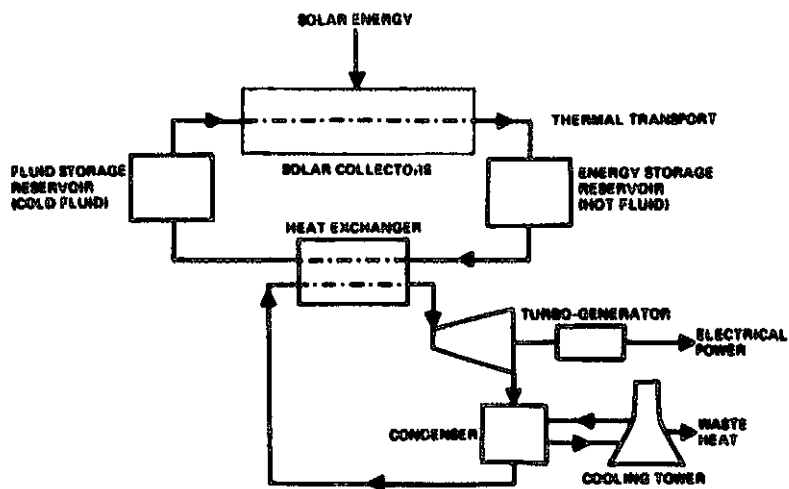


Fig. 2

## MITRE PHOTOVOLTAIC ENERGY SYSTEM STUDY

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### Presentation Summary

The MITRE Corporation is making recommendations to the National Science Foundation on solar energy research programs, including a program for photovoltaic energy systems. MITRE has been asked to make a system analysis study for each program and then formulate a program development plan, detailed and specific proof-of-concept experiments, and a utilization plan for each.

Figure 1 shows various types of options for photovoltaic systems that are being considered in the MITRE study. Those interconnected by the heavy lines would be included in the type of system shown in Fig. 2. Such a large centralized system would use solar energy to produce both electricity and hydrogen fuel gas, to supplement smaller distributed household systems of the same type. The hydrogen could also be used for energy storage, for instance by storing it in depleted natural gas wells. The DC electric power that would be generated by the solar cell array would be transmitted directly to the electrolysis facilities for the production of hydrogen and oxygen, or would be converted to AC power and distributed to households, industrial facilities, and other electricity consumers. The electrolysis facilities would convert water, taken from the ocean or other sources, to hydrogen and oxygen gases, which would be transmitted and distributed by pipelines to storage facilities or directly to fuel gas consumers, including, if required, fuel cells or other facilities for converting the energy back to electricity.

Some of the advantages and disadvantages of such solar-cell/hydrogen-fuel systems are summarized in Fig. 3.

Some of the major technical and economic problems that must be resolved, before systems of this type can be implemented on a large scale, are shown in Fig. 4. One of the major requirements is to reduce the present cost of silicon solar cells so that they would be competitive with other types of solar energy collectors. This might be accomplished not only by simplifying present production techniques but also by developing new low-cost solar cell designs and introducing new techniques for the mass-production of these cells.

Figure 5, which is based on learning-curve experience for silicon solar cells and other solid state devices, indicates that, starting with the solar-cell industry's current production of 50 kilowatts per year, if production rates are doubled each year, and adequate R&D funding is provided, the price of silicon solar cells might be expected to be driven down at a rate of between 20 percent and 30 percent per year. The cumulative power capacity of silicon solar cells that would be produced under this type of scenario, as well as cumulative production costs, under these conditions, is shown in Fig. 5.

Figure 6 compares the estimated cost of electricity for various types of plants, assuming that the plants would be constructed in the year 2000 and operated over the period 2000 to 2020. These estimates are based on data provided by the Federal Power Commission and others, and are given in terms of dollars inflated to correspond to the periods shown. Details on the assumptions used in these calculations are given in the footnotes to Fig. 6.

### Discussion

(Not recorded)

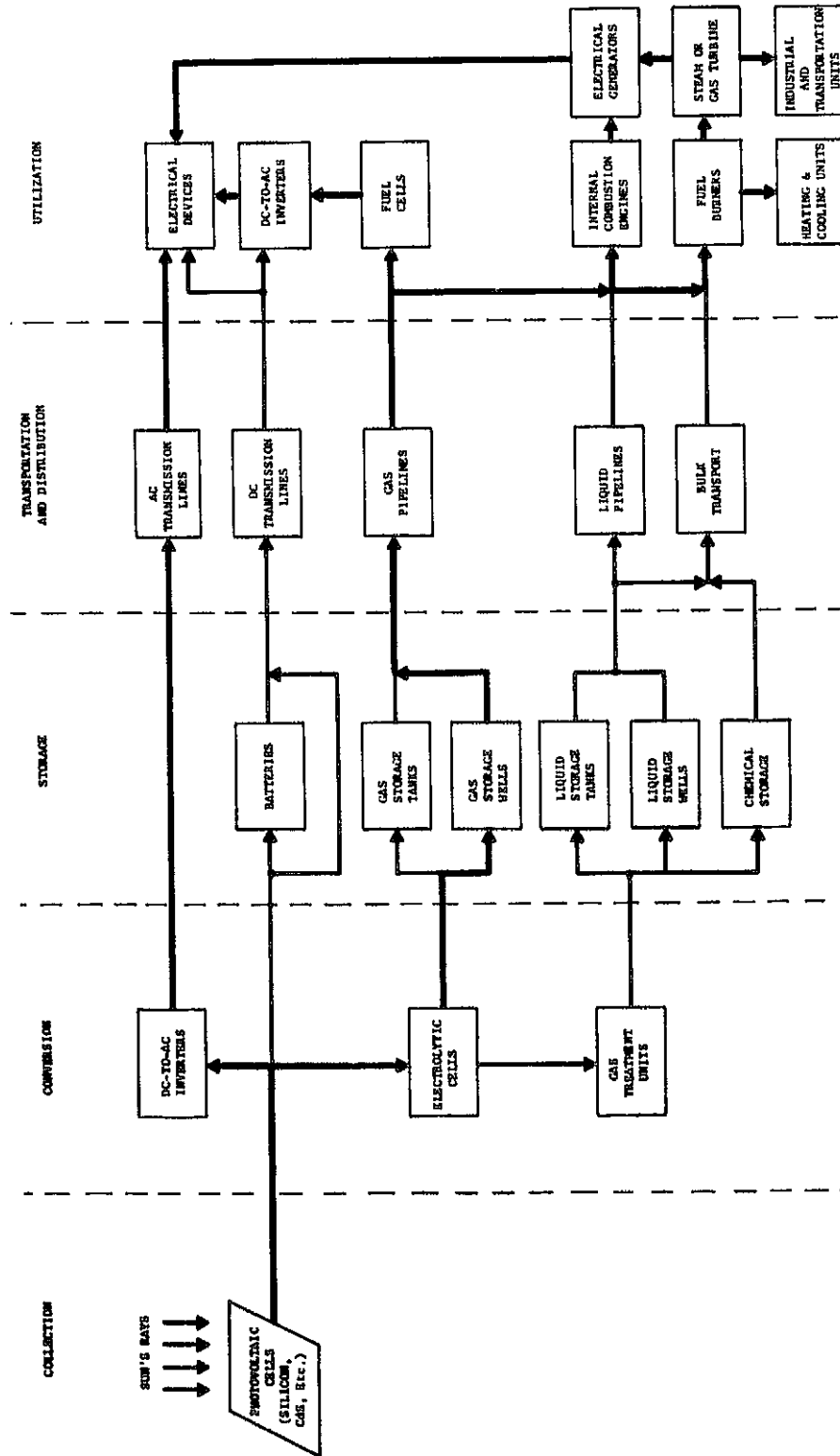


Fig. 1

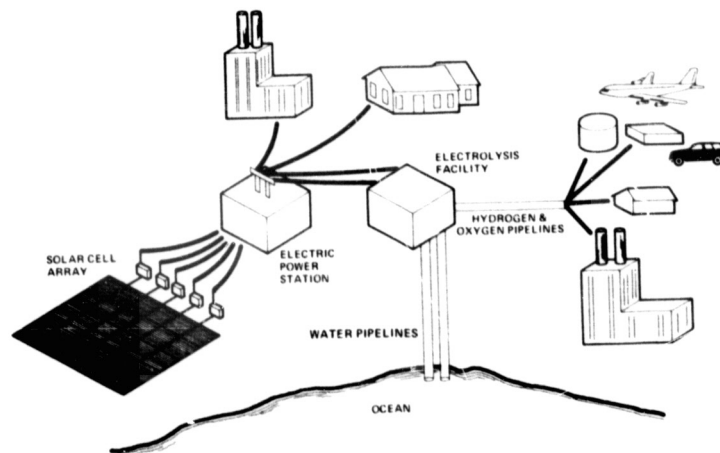


Fig. 2

ADVANTAGES

- HIGH RELIABILITY OF COLLECTOR SYSTEM
- LOW-TEMPERATURE OPERATION
- LONG LIFE OF SILICON SOLAR CELLS
- NO MOVING PARTS
- NO VACUUM REQUIRED
- NO HARMFUL WASTE-PRODUCTS OR POLLUTION
- DEGALINATED WATER SUPPLY PROVIDED
- GLOBAL HEAT BALANCE MAINTAINED

DISADVANTAGES

- PRESENT HIGH COST OF SOLAR CELLS
- PRESENT LOW EFFICIENCY OF SOLAR CELLS
- EXTENSIVE USE OF LAND

Fig. 3

- DECREASE COST OF SILICON SOLAR-CELLS
- IMPROVE EFFICIENCY OF SOLAR ENERGY COLLECTION
- MODIFY PIPELINES FOR HYDROGEN
- DEVELOP SUITABLE METHODS FOR STORING HYDROGEN
- DEVELOP DEVICES AND PROCESSES FOR UTILIZING HYDROGEN

Fig. 4



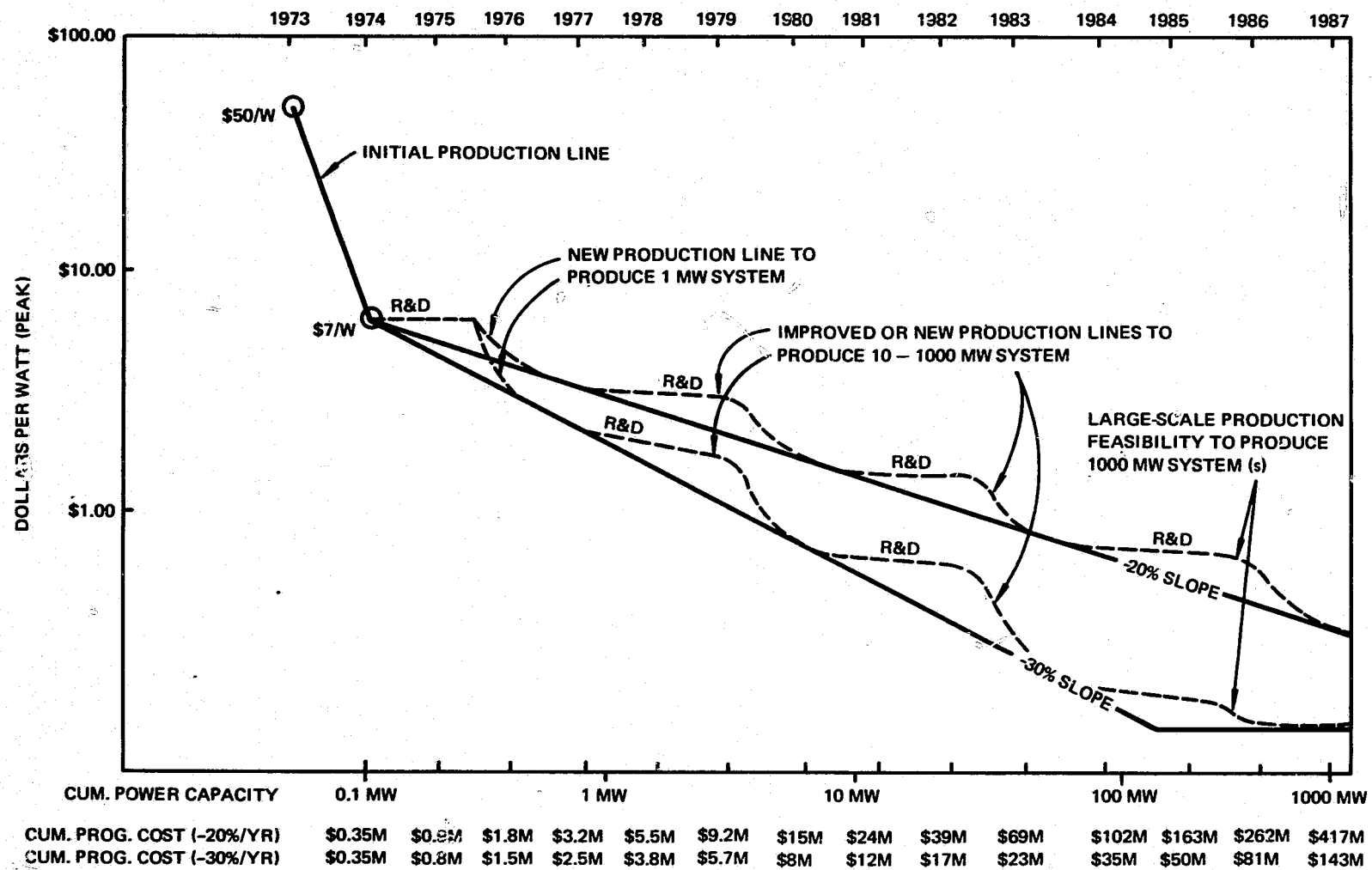


Fig. 5

SESSION III. SYSTEMS AND DIAGNOSTICS - ELDRIDGE

TYPE OF SYSTEM	INITIAL INVESTMENT, POWER GENERATION	FUEL COSTS <sup>5</sup>	INITIAL INVESTMENT, CONVERSION & STORAGE	OTHER COSTS	TOTAL 20 YEAR COST	PLANT FACTOR	AVERAGE COST OF ELECTRICITY AT PLANT
	YEAR 2000	YEARS 2000 TO 2020	YEAR 2000	YEARS 2000 TO 2020	YEARS 2000 TO 2020	YEARS 2000 TO 2020	YEARS 2000 TO 2020
HYDRO-ELECTRIC	\$392 TO <sup>1</sup> \$1230/KW			\$761 TO \$2398/KW	\$1153 TO \$3628/KW	0.60	11.1m/KWH TO 34.5m/KWH
GAS FIRED	\$392/KW <sup>1</sup>	\$2451/KW		\$1143/KW <sup>7</sup>	\$3986/KW	0.60	38.1m/KWH
OIL-FIRED	\$458/KW <sup>1</sup>	\$2451/KW		\$1336/KW <sup>7</sup>	\$4245/KW	0.60	40.5m/KWH
COAL-FIRED	\$442/KW <sup>2</sup>	\$1666/KW		\$1294/KW <sup>7</sup>	\$3402/KW	0.60	34.1m/KWH
NUCLEAR-FUELED	\$560/KW <sup>3</sup>	\$412/KW <sup>6</sup>		\$1948/KW <sup>8</sup>	\$2920/KW	0.60	28.1m/KWH
PHOTOVOLTAIC (WITHOUT STORAGE)	\$368/KW <sup>4</sup>			\$1085/KW <sup>9</sup>	\$1453/KW	0.25	32.6m/KWH
PHOTOVOLTAIC (WITH H <sub>2</sub> STORAGE)	\$368/KW <sup>4</sup>		\$328/KW	\$2051/KW <sup>9</sup>	\$2747/KW	0.25	61.9m/KWH
PHOTOVOLTAIC PLUS WIND ENERGY (WITH H <sub>2</sub> STORAGE)	\$305 TO \$369/KW		\$105/KW	\$1150 TO <sup>5</sup> \$1480/KW	\$1560 TO \$1874/KW	0.275	32.2m/KWH TO 38.6m/KWH

<sup>1</sup>CHERRY DATA FOR 1968 ("GENERATION OF POLLUTION-FREE ELECTRICAL POWER FROM SOLAR ENERGY", ASME PAPER NO. 71-WA/SOL-2) ADJUSTED TO 1970 BY FACTOR OF 1.07 THEN ADJUSTED TO YEAR 2000 BY FACTOR OF 2.45

<sup>2</sup>SIMPSON DATA FOR 1965 ("THE CASE FOR NUCLEAR ENERGY", IEEE SPECTRUM, SEPTEMBER 1972) ADJUSTED TO 1970 BY FACTOR OF 1.14 PLUS POLLUTION CONTROL COST OF \$58/KW (FROM SIMPSON, IBID). THEN ADJUSTED TO YEAR 2000 BY FACTOR 2.45.

<sup>3</sup>CHERRY DATA FOR 1968 (IBID) ADJUSTED TO 1970 BY FACTOR OF 1.07 PLUS POLLUTION CONTROL COST OF \$15/KW (FROM SIMPSON, IBID) THEN ADJUSTED TO YEAR 2000 BY FACTOR OF 2.45

<sup>4</sup>ASSUMES INVESTMENT COST OF \$2.70 PER SQUARE FOOT (1970 DOLLARS) FOR SOLAR CELL ARRAY, 4% EFFICIENCY, 45 LIGHT CONCENTRATION.

<sup>5</sup>FUEL COSTS BASED UPON FPC 1968 DATA, ADJUSTED TO 1970 BY FACTOR OF 1.07, AND ADJUSTED TO YEAR 2000 TO 2020 USING SCENARIO. PLANT EFFICIENCY IS ASSUMED TO BE EQUAL TO 10.2 M BTU/MWH  
20 YR PRODUCTION (1.6) (18760) (20) (1) = 106.120 MWH = 1072.2 MBTU

	COAL	OIL	GAS
FPC 1968	25.5¢/MBTU	32.8	26.1
1970	27.3	35.1	26.9
1975	32.75	44.1	61.9
1985	41.0	63.2	67.3
2000	54.6	80.7	60.7

<sup>6</sup>FUEL COST FOR NUCLEAR, IN 1970 DOLLARS, IS ASSUMED TO BE CONSTANT OVER TIME.

<sup>7</sup>BASED ON FIXED CHARGE RATE GIVEN IN FPC (1-19-6)

COAL, OIL, AND GAS - 14.2% PER YEAR  
HYDRO-ELECTRIC - 9.7% PER YEAR  
NUCLEAR - 14.7% PER YEAR  
NUCLEAR FUEL - 12.4% PER YEAR

O&M COST RATES BASED UPON FPC DATA, I.E. \$3.00 PER KW, ADMINISTRATIVE AND GENERAL EXPENSES \$ 75/KW, AND WORKING CAPITAL \$3.4% (10.2%) (INVESTMENT) (20) = .069 (INVESTMENT)

COST OF CAPITAL  
% OF INVESTMENT NEEDED PER WORKING CAPITAL

<sup>8</sup>ASSUMED LIFE OF NUCLEAR FUEL - 5 YEARS.

<sup>9</sup>BASED ON FIXED CHARGE RATE OF 9.7% PER YEAR (I.E. SAME AS HYDROELECTRIC, SEE ABOVE)

Fig. 6

## SOLAR THERMAL CONVERSION MISSION ANALYSIS

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### Presentation Summary

The Civil Programs Division of The Aerospace Corporation is under contract with the National Science Foundation to conduct a Mission Analysis of Solar Thermal Conversion Systems. Although the subject of this study is solar thermal conversion, many of the issues and study results will be pertinent to photovoltaic conversion, which is the subject of this workshop. At this time, we are approximately three weeks away from being able to draw a significant number of conclusions. Therefore, I will review for you the objectives and scope of our study, briefly describe part of the methodology which will indicate what is meant by a mission and, finally, discuss one of the results that may be of particular interest to photovoltaic system designers.

Figure 1 indicates the objective and scope of our study. First, we are to formulate a methodology to examine solar thermal conversion missions and, second, to apply this methodology to Southern California for the time period 1980 to 2000. By missions, we are referring to alternative applications or families of applications. For example, a solar thermal conversion system might provide electrical service, or, it might provide combined electrical and thermal service. The solar power system might be a large remote central station powerplant or a smaller municipal-sized plant closer to the load center. It might be sized to serve a community such as is typically served by a sub-station, or, the solar power system might be placed at individual load centers, such as houses or shopping centers.

We expect the results of this analysis to provide a basis for selecting the preferred missions and systems for solar thermal conversion, and establish technical and economic bounds for systems, subsystems, and components. Finally, we plan to determine the market capture potential for solar thermal conversion within the preferred missions, and estimate the impact on our national resources.

Figure 2 illustrates several issues and the methodology of the mission analysis. Frequently in a "systems" examination of solar power the effort has involved balancing the incoming insolation energy with the load. Much of the effort is directed at selecting the proper subsystems such as the collectors and storage subsystem. In some cases, it is very difficult to balance the insolation and loads, and energy is drawn from conventional power sources to make up any differences.

Figure 3 illustrates one of the results of the mission analysis study that may be of particular interest to photovoltaic system designers. This slide shows the map of Southern California, bounded by the Pacific Ocean, the Mexican border, the Colorado River, the Nevada state line, and on the north by the boundary of the Southern California Edison service area. Within this region are shown eight different climatological subregions as identified by the Weather Bureau. In our study, we have collected all available data on the solar insolation in these subregions and for Albuquerque, New Mexico, to prepare models for use in system design studies. This data is recorded on magnetic tape and specifies, for each hour of a two-year period, a complete set of insolation and weather data. It is planned to use one or more of these models as a reference standard in the solar thermal conversion part of the NSF program. These tapes may be made available to photovoltaic system designers through NSF to facilitate comparisons between systems.

In addition to the eight climatological subregions in Southern California, we have also prepared a tape for Albuquerque, New Mexico. In many instances there were no measurements in the subregions of some of the quantities of interest to solar thermal system designers. For example, there were no measurements of the direct or unscattered insolation. Where this situation was found to exist, we have estimated the appropriate values. These

estimates are based upon regression analyses of measurements at other locations such as at Albuquerque. In some regions only weather data is available, and all insolation values must be estimated. Wherever a value has been estimated, this is indicated on the magnetic tape.

Figure 4 summarizes the type of data stored on the tape of each model. Hourly data, including total and direct insolation, are given for at least one year and, in most cases, for two years. The location of the subregion station and the position of the sun are specified. Temperature and other weather parameters are included where available. All of this data has been compiled in a single format. Should you wish to use this data as part of an NSF contract or grant, arrangements should be made through your NSF program monitor.

In the mission analysis, the emphasis is not a single system but on the multitude of units in a regional power system which might include several solar plants as well as a large number of conventional plants. The study is concerned with the interaction of these systems, particularly the constraints that might be imposed upon the solar plant by the conventional plants.

An example of such an interaction is derived from the reliability requirements imposed by all major utility systems. Besides the repetitive daily and seasonal variations in the insolation, there are also periods of poor weather with little or no insolation. This situation can be considered as the equivalent of a forced outage for a conventional plant and can be compensated for in solar plants by providing a large energy storage subsystem. Unfortunately, energy storage is costly and may be impractical in some situations. In this case, the forced outage rate of the solar plant might be larger than for a similar conventional plant. The utility would then have to increase the generating capacity margin to provide the same degree of reliability. Margin is the excess of the generating capacity over the peak demand. The ability of a solar plant to displace a conventional plant while maintaining equal reliability for the total utility system is what we have called "capacity displacement."

Once a utility has built a solar plant, it is reasonable that it would be operated whenever possible. This is because the fuel is essentially free, and the solar plant would probably have the minimum incremental or marginal cost. This will result in a saving of the conventional plant fuels and is what we have called "energy displacement."

If the capacity displacement of a solar plant is found to be too low due to weather outages, it is possible that two or more plants, placed at different sites and of equivalent total size, would be preferred. This result depends on the statistical independence of insolation outages at the solar plant sites.

Another correlation of interest is that between the insolation and the demand. If there is a correlation between periods of poor insolation and reduced demand, as is the case in California in the winter, then the insolation reductions would be less important.

## Discussion

(Not recorded)

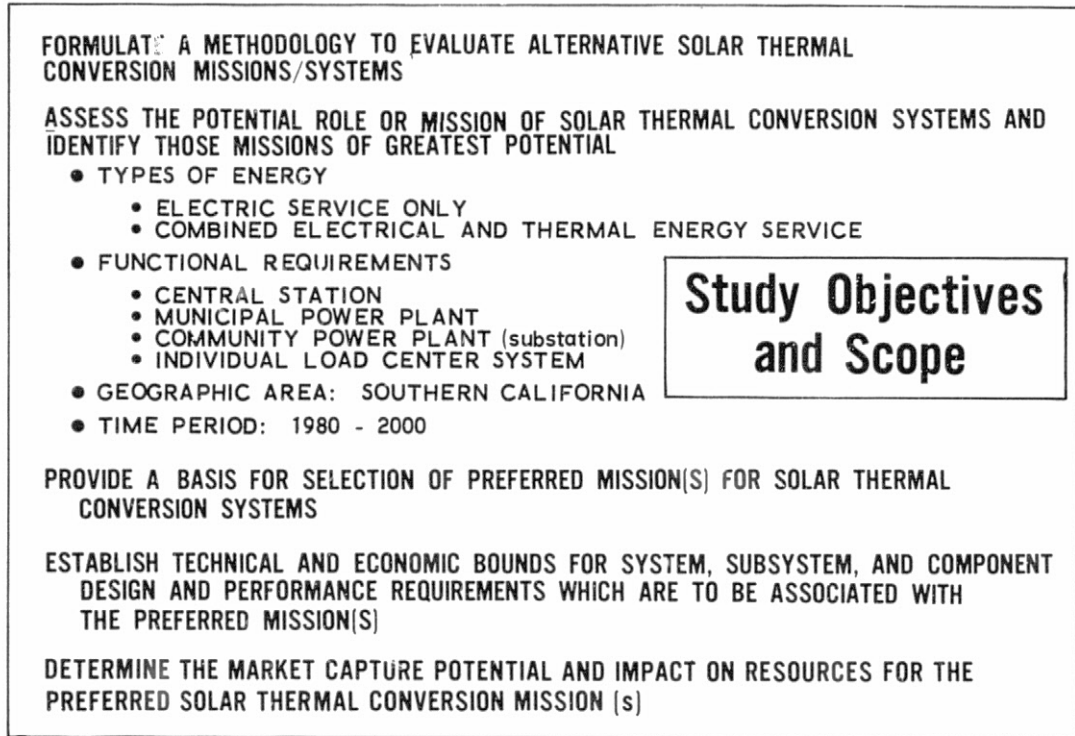


Fig. 1

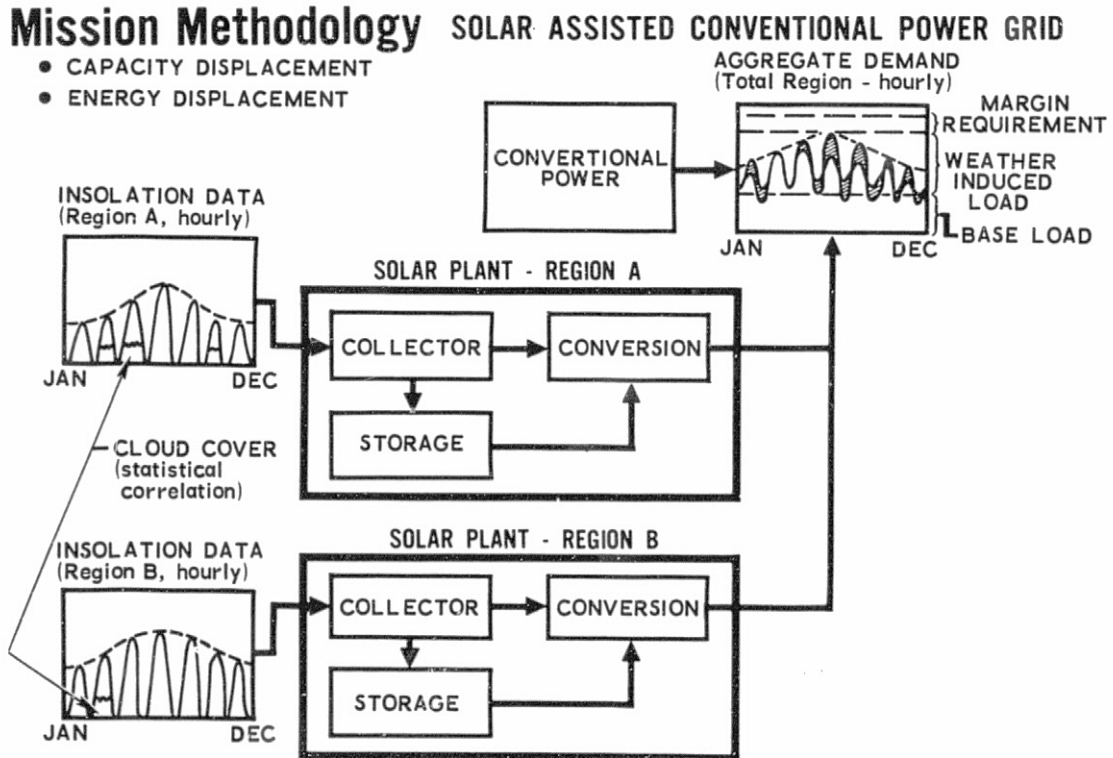


Fig. 2

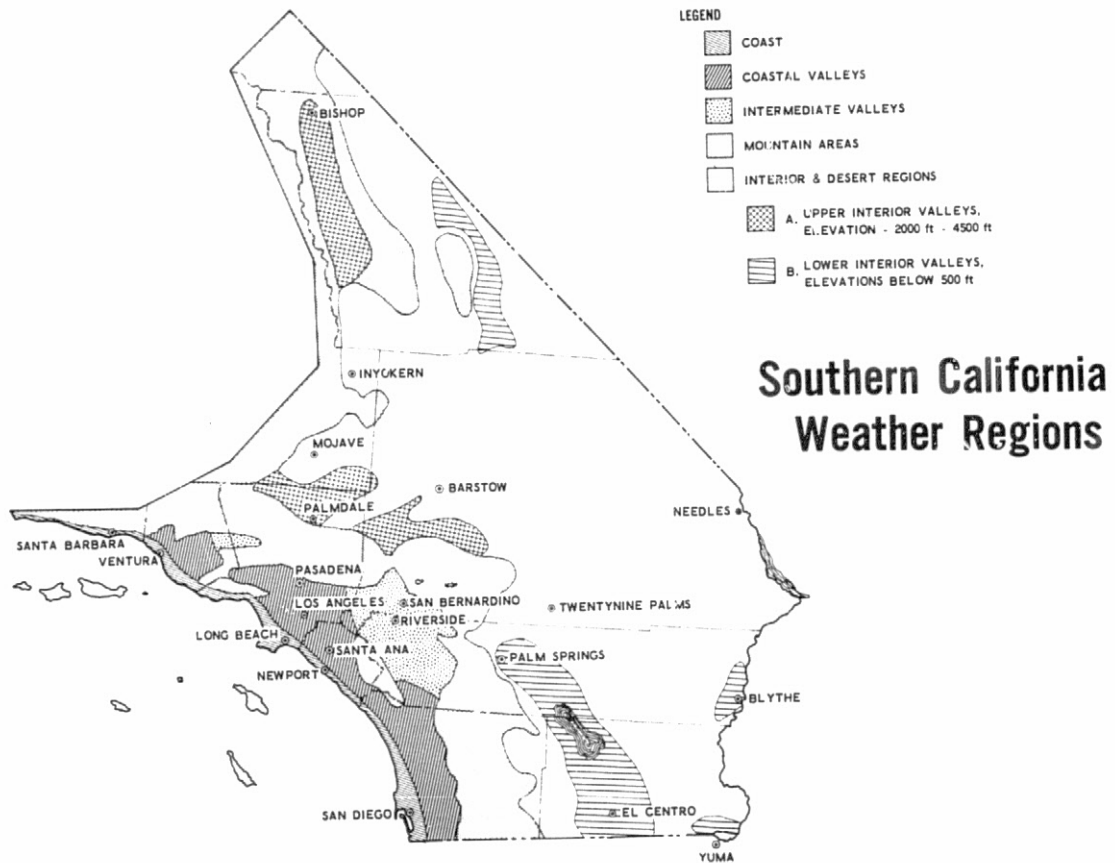


Fig. 3

## Insolation Data Base Characteristics

- HOURLY
- SEPARATE TOTAL AND DIRECT INSOLATION
- 1 YEAR MINIMUM COVERAGE
- REPRESENTATIVE OF MAJOR SOUTHERN CALIFORNIA REGIONS
- TEMPERATURE AND OTHER SURFACE WEATHER INFORMATION
- UNIFORM FORMAT - BASED ON DECK 280

Fig. 4

## PHOTOVOLTAIC SYSTEM MODEL FOR TERRESTRIAL APPLICATIONS

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### Presentation Summary

Pre-design studies and design tasks for photovoltaic systems or subsystems for terrestrial solar energy applications require a considerable degree of sophistication, if they are to yield anything but rough estimates. These design tasks differ from similar ones which have been carried out for space power systems, since:

- (1) The loads are uncontrolled and, at best, a statistical sum.
- (2) The input intensity and the spectral distribution vary randomly.
- (3) The input radiation contains both collimated and scatter components.
- (4) Array temperature is determined by the ambient air temperature rather than a radiation balance.
- (5) Solar cell spectral response varies with temperature, and, since the incident spectral distribution varies, a simple temperature correction on light-generated current is no longer feasible.

Based on these requirements, a complete computer simulation of the photovoltaic system has been developed. Only a few of the system's key features can be listed here:

- (1) The program is structured in subprograms on a subsystem and component basis to provide maximum adaptability (Figs. 1 to 3).
- (2) As far as practical, the simulation is based on a full description of established underlying phenomena. This includes atmospheric modification of the solar spectral distribution, the spectral response and the current-voltage characteristic of solar cells, characteristic of storage batteries, etc.
- (3) Summary experience factors such as the "packing factor" for solar cells on the array, the "assembly loss" factor (array output relative to sum of individual cell outputs), etc., are included.
- (4) All potential design variables are available as input variables.
- (5) Various operating modes are provided, such as resistive loads, constant voltage operation such as with battery buffer, or maximum power point tracking.
- (6) The system can be operated as single runs or for simulated continuous operation over extended time periods at selectable intervals as short as 10 min, using the load and solar input data provided for each time interval.
- (7) The system can operate off available Weather Bureau tapes with hourly insolation data.
- (8) For a given array area, design voltage, and minimum acceptable cell voltage, the numbers of cells to be series connected and parallel connected in the array are determined.
- (9) Outputs of energy used, energy delivered by solar array and by auxiliary supply, change in battery storage and total charge stored are provided for each time interval and as daily totals; most intermediate results are available on special command.
- (10) Outputs can be tabulated and plotted.

The system was first designed for the evaluation of the characteristics of residential photovoltaic systems. Figure 4 shows a computer plot of a 2-day run, using recorded power load data from a suburban residence with 2 unit air conditioners and above average power consumption. The 2 days were a Saturday and Sunday at the beginning of a sequence of extremely hot summer days in a recent year. Since hourly insolation data are not available for the particular dates, 2 days of recorded Weather Bureau data from a weatherwise similar sequence of days from Washington, D.C. (June 21-22, 1957) were picked for the insolation and air temperature data. The horizontally mounted array of 40-m<sup>2</sup> area and the storage battery (lead acid) of 30-kWh capacity with 50 percent depth of discharge analyzed in the data of Fig. 4 are capable of supplying approximately 50 percent of the particularly large load (about twice average) on these particular days.

For a comparative study, carried out by another group, of the potential benefits of the use of photovoltaic arrays to supply peak power in a typical utility system of 5000 MW capacity, but equipped with load leveling batteries of a new type, a slightly modified subroutine STORE was prepared. In this system, battery charging is limited by inverter capacity, and the priorities for load allocation were to follow increasing generation costs in the sequence: photovoltaic solar array, base generating capacity, battery, gas turbine. A run of the program for the same 2 days as used for Fig. 4, using actual utility load data, provided the required data for the study (Fig. 5). The systems performance data required for this analysis could not have been obtained without availability of the program.

Input data used in photovoltaic systems analysis are given in Table I.

### Discussion

Q: Why do you simulate the thermal loads rather than doing an actual experiment?

A: People in the construction industry feel that they have to run a simulation of the building which they intend to build for a whole year or two with actual Weather Bureau data in order to really evaluate how the building will perform. I feel that one should be able to select certain sequences of days to follow the performance of the systems through in an analytical way like this where you want, for different seasons, for instance, to dictate which are close to an average or to the extremes in both ways. You then select from the available data for the various climate regions certain day sequences which you want to evaluate. Once you have a program, it's a relatively simple thing to run it. Probably it is a lot less costly than an experimental program.

C: I would like to call your attention to a computer program developed by the National Bureau of Standards.

A: We have it.

Q: You have it?

A: That's the thermal load of the building.

Q: To what extent is your program available for various simulations?

A: I think we would be very willing to help you in analyzing systems problems. We don't have all of the software written up or instructions, and so on, and we are also continuously improving and expanding on it. But just as we are helping Philadelphia Electric Company with it, as I have just mentioned, we are very willing to help others in doing analysis, also.

Q: We also are running systems simulations and to us Saturdays and Sundays are the lowest-load days of the week; Mondays through Fridays are the days to look at. Why did you pick Saturday and Sunday?

A: I think they were picked by Philadelphia Electric. Saturday is reasonably a high-load day and Sunday is a low-load day and we really didn't use all of the base-load capacity.

Q: Have you included a day of no sunshine?

A: No, this study had just 2 days in which we presented a very high summer peak load in Philadelphia, but we can pick any other days and we have for other evaluations. For Philadelphia, we don't have any Weather Bureau data available which contains insolation, so we use Washington, D.C., Weather Bureau data and pick sequences of days which seem similar to days at some other time in Philadelphia where we have little data available.



- C: I think I should say something here. We tried to do the very same thing and tried to get a correlation with the data which we could get from Greater Wilmington Airport, which isn't so far away from the position of Solar One, and at times we got almost anti-coincidence. It is a matter of micro-climate versus macro-climate, and I think that is a very good point for the actual position where you have your house.
- A: It is rather unsatisfactory to work with presently available data. One hopes that in future years, we will have data which are (1) available for many more localities and (2) really representative of spectral distributions that we are dealing with, such as percent water, dust content, and so on.

Table 1. Input Data Used in Photovoltaic Systems Analysis

Subsystem	Quantity	System		Unit
		Residential	Utility	
Solar array	Area	40	$11 \times 10^5$	m <sup>2</sup>
	Packing factor	0.9	0.9	-
	Assembly loss	0.06	0.06	-
	Design voltage	130	1050	V
	Mtn. cell voltage	0.40	0.40	V
Regulators	Bus voltage	120	1000	V
	Efficiency:			
	Bus regulator	0.9	0.93	-
	Charge regulator	0.95	0.93	-
	Discharge regulator	0.85	0.93	-
Battery	Capacity	30	$42 \times 10^5$	kWh
	EMF	.10	653	V
	Polarization	10	57	V
	Charge gradient	1.27	397	V
	Internal resistance	0.1	$5.68 \times 10^{-5}$	$\Omega$
	Depth of discharge	0.25	0.02	- <sup>*</sup>
	Max. charge	0.9	1.0	- <sup>*</sup>
	Night charge stop	0.5	1.0	- <sup>*</sup>
Auxiliary system	Base generation	N.A.	$39 \times 10^5$	kW
	Gas turbine capacity	N.A.	$5 \times 10^5$	kW
	Inverter rating:			
	Charging	N.A.	$6.10^5$	A
	Discharging	N.A.	$3.5 \times 10^5$	A
	Night rate start	Cont.	N.A.	h
	Night rate end	Cont.	N.A.	h
Charge at beginning of run	8	$0.7 \times 10^5$	kWh	
Atmospheric absorption	Date	20.6.1957	20.6.1957	-
	Number of days	2	2	-
	Atm. pressure	760	760	torr
	Ozone	2.5	2.5	mm
	Dust	300	300	cm <sup>-3</sup>
	Precip. water	compute	compute	mm

\*Capacity fraction of.

Table 1 (contd)

Subsystem	Quantity	System		Unit
		Residential	Utility	
Atmospheric absorption (contd)	Wavelength:			
	Min	300	300	nm
	Max	1100	1100	nm
	Interval	50	50	nm
Location	Latitude	40	40	$^{\circ}$ N
	Tilt	0	40	$^{\circ}$ S
	Rotation	0	0	
Time	Start	0.0	0.0	h
	Interval	60	60	min
Solar cell	Thickness	300	300	$\mu$ m
	Junction depth	0.4	0.4	$\mu$ m
	Mobility:			
	Base	1250	1250	$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$
	Diff. region	40	40	$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$
	Carrier conc:			
	Base	$10^{15}$	$10^{15}$	$\text{cm}^{-3}$
	Diff. region	$10^{19}$	$10^{19}$	$\text{cm}^{-3}$
	Surface recomb:			
	Base	$10^8$	$10^8$	$\text{cm s}^{-1}$
	Diff. region	0.1	0.1	$\text{cm s}^{-1}$
	Minority carrier:			
	Lifetime			
	Base	10	10	$\mu$ s
	Diff. region	4	4	$\mu$ s
Drift fields	None	None		
Light exposed area	1.0	1.0	$\text{cm}^2$	
Junction area	1.0	1.0	$\text{cm}^2$	
Series resistance	0.5	0.5	$\Omega$	

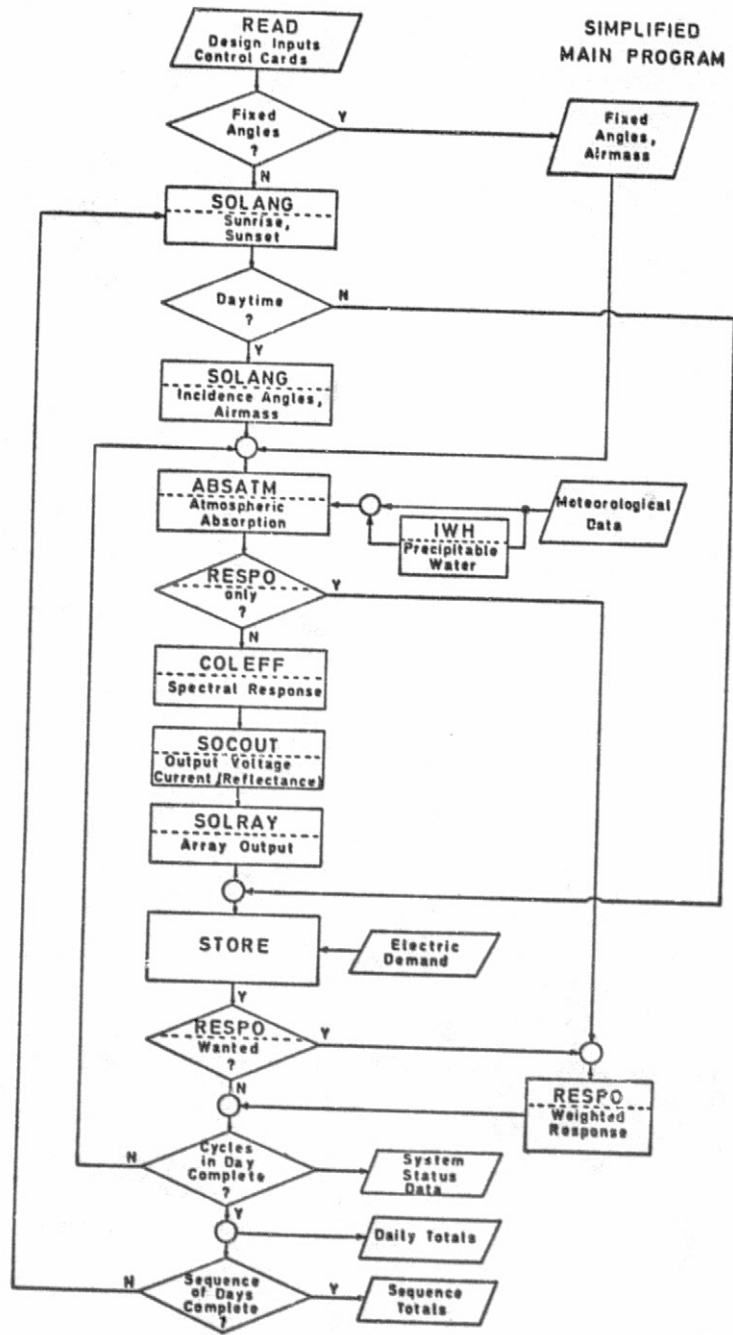


Fig. 1

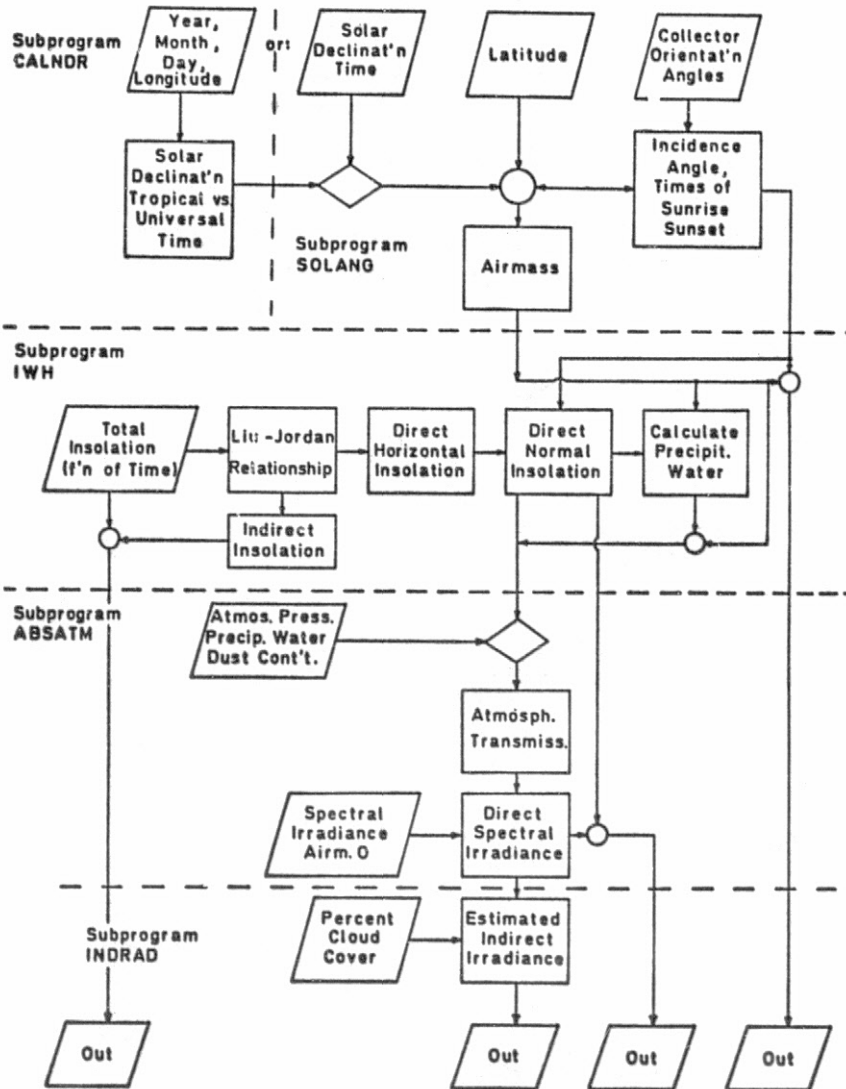


Fig. 2

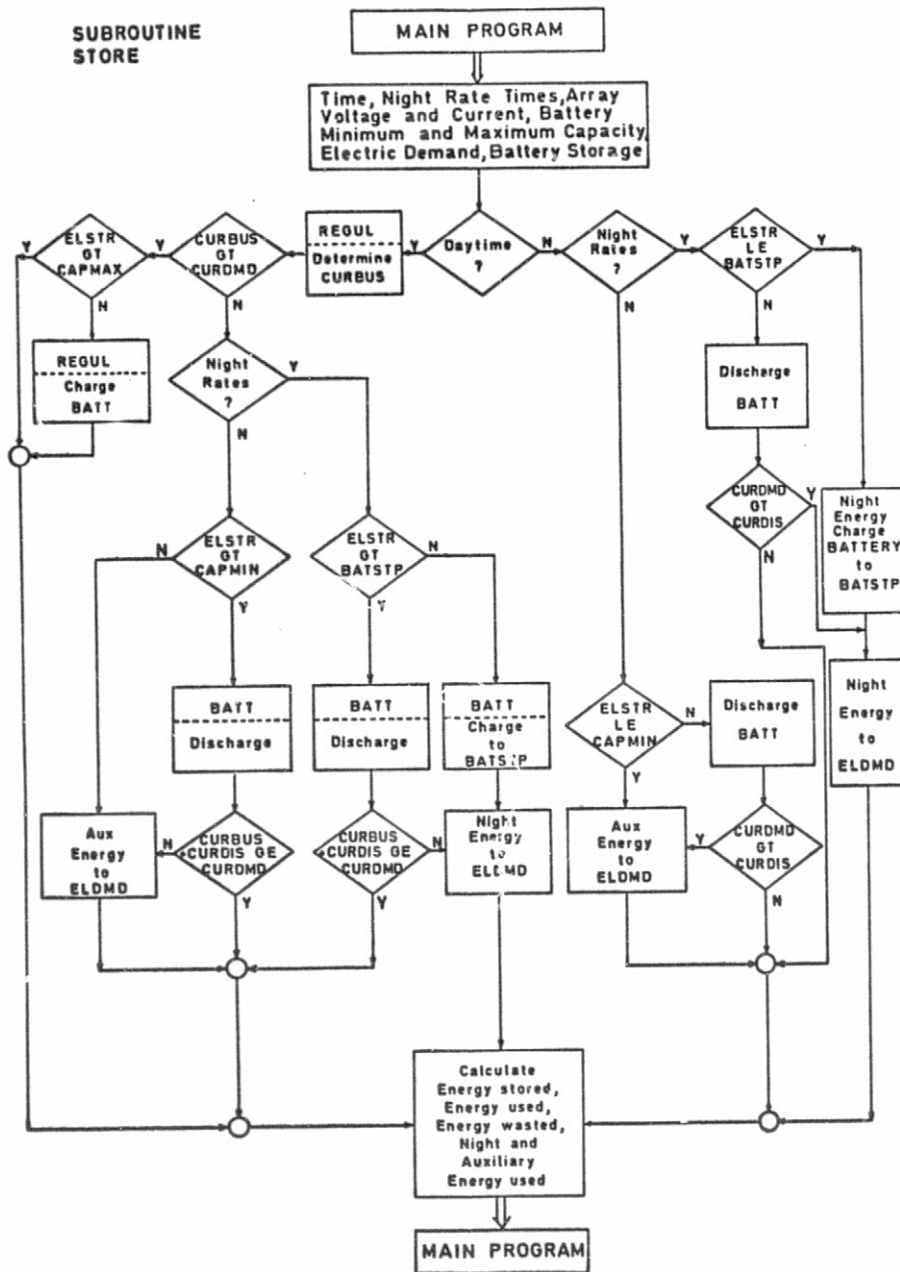
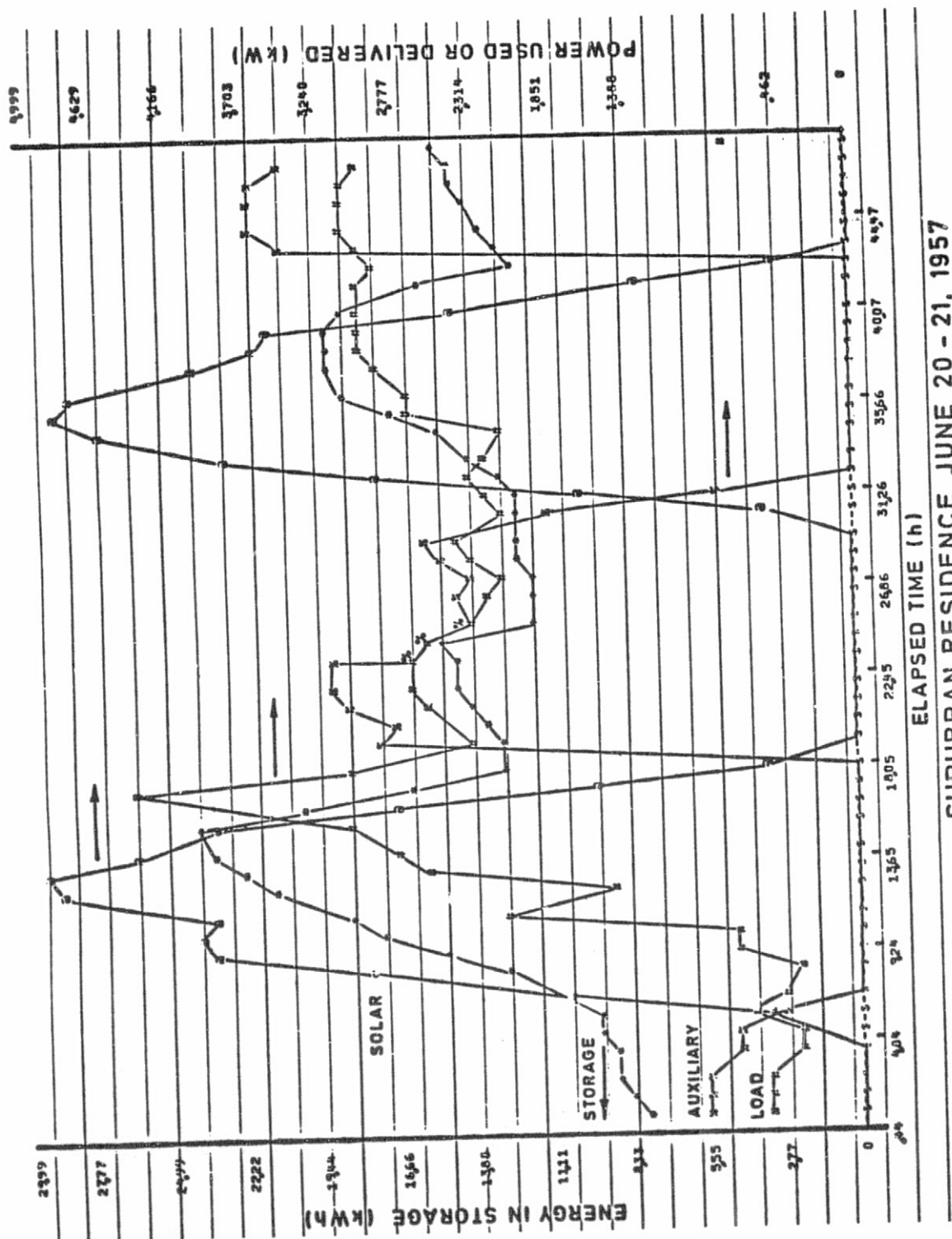
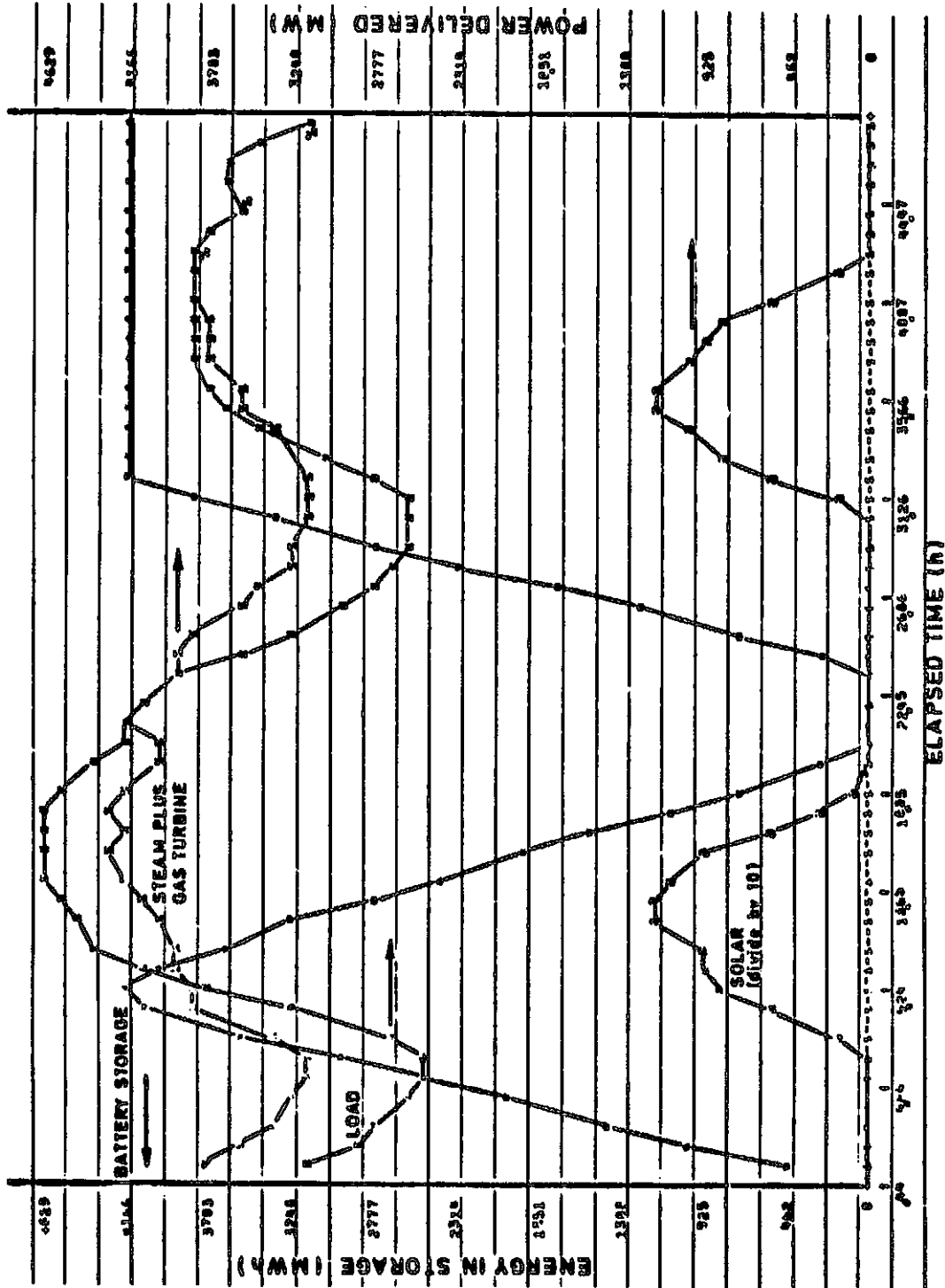


Fig. 3



SUBURBAN RESIDENCE JUNE 20 - 21, 1957

Fig. 4



UTILITY SYSTEM WITH BATTERY AND SOLAR ARRAY JUNE 20 - 21, 1957

Fig. 5

## SATELLITE SOLAR POWER STATION (SSPS) POWER SYSTEM INTEGRATION

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### Presentation Summary

#### Introduction

The basic concept of the Satellite Solar Power Station (SSPS) is to collect and convert (at synchronous orbit) solar energy into microwave energy for transmission to the earth, as shown in Fig. 1. The solar energy is converted via silicon photovoltaic collection devices into high-voltage dc required for the operation of the microwave amplifiers. The all-weather microwave power beamed to the earth is rectified and converted back to dc power for terrestrial applications. A four-company study team of A. D. Little, Grumman, Raytheon, and Textron/Spectrolab has been investigating this concept for over two and a half years and has continually modified and improved the preliminary design of the SSPS. The present baseline SSPS produces 8000 megawatts in orbit and 5000 megawatts on the earth, with the orbital platform measuring  $11.73 \times 4.33$  km.

The baseline configuration consists of two concentrator-type solar collectors with a single microwave transmitting antenna positioned between them. A support structure extending the full length of the vehicle provides bending and shear continuity. This configuration is shown in Fig. 2.

The solar collectors each have 10 longitudinal corrugations or troughs extending the full length of the collector. Each trough consists of a 210-m (690-ft) solar blanket, on either side of which is positioned a selectively coated reflecting mirror angled at 60 deg to the blanket surface. The longitudinal elements of the vehicle support structure form the framework for the mirrors, while the lateral elements act as conductive busses for transfer of dc power from the solar blankets to a central buss/mast.

Bearings and brush-type slip rings at the collector edges nearest the antenna provide power transfer from the fixed buss/mast to the rotating antenna mast.

Interference with the microwave beam by the structure between the solar collector is minimized by fabricating this structure from a low loss dielectric material with the element shapes configured to reduce beam attenuation and scatter.

#### General

A key driver in designing this orbital platform is maximizing the power-to-weight ratio. The solar array bus structure and mast represent approximately 30 percent of the total orbital weight, as shown in Fig. 3, and study emphasis has been put into this area. The requirements of a weight optimum power distribution system were determined and were then integrated with the structural requirements and the thermal environment of the SSPS.

A weight optimization analysis was performed to determine the preferred operating voltage and transmission efficiency for the SSPS power distribution system. In addition, an assessment was made of the options for transferring power across the rotating joints between the solar collector assemblies and the antenna.

The weight optimization analysis (summarized in Fig. 4) showed that operating voltages of about 60-80 kV provide the highest power-to-weight ratios; however, a 40-kV system was selected for the baseline as being the upper limit of compatibility with the microwave power generating system.



The power transmission efficiency analysis considered the weight implications both of the bus cross-section area needed to provide a given efficiency and the additional solar collector area needed to compensate for transmission losses. For a 5000 mw, 40-kV system, the peak power-to-weight ratio is achieved at a 90.5% efficient transmission system as depicted in Fig. 5.

Figure 6 illustrates the relative motions of the solar arrays and microwave antenna needed to maintain their correct orientation toward the sun and the ground station. A flight mode with the X axis normal to the orbit plane requires that the antenna rotate 360 deg per day about the X axis to stay pointed at the ground station. The solar arrays must rotate once a year about the X axis to maintain sun pointing and, in addition, must "nod" through an angle of  $\pm 23\text{-}1/2$  deg to compensate for the changing angle of the orbit plane with respect to the plane of the ecliptic.

An assessment was made of the options for transferring power across the rotating joints between the solar collectors and antenna as shown in Fig. 7. Principal characteristics of the problem are low rotational speeds and large amounts of power. In assessing the options, prime considerations were reliability, compatibility with the environment, and lack of complexity. The straightforward approach of slip rings and brushes appeared to be most compatible with the requirements and was therefore selected for the baseline configuration.

Figure 8 summarizes the power distribution characteristics for the baseline configuration. However, it should be noted that the 40-kV system voltage is not the most weight effective. Operating voltages in the 60- to 80-kV range offer power/weight ratio advantages and should be further examined.

To keep orbital weight down, maximum use must be made of the power distribution system in designing the SSPS structural framework. To do this, however, we must reconcile the conflicting requirements of the power distribution system and the structure. These requirements can be summarized as follows:

The power distribution system needs:

- (1) A low resistivity material for the conductors.
- (2) A maximum ratio of surface to cross-sectional area of conductor material to keep the working temperature down and maintain high efficiencies.
- (3) A good view of space to ensure adequate heat dissipation.
- (4) Adequate spacing between busses to minimize electromagnetic effects between parallel currents.
- (5) Absence of gaseous contamination, which could promote arcing.

The structural system needs:

- (1) Lightweight high-strength materials.
- (2) Ability to handle internal loads induced by tension pulls and warping of solar cell blankets, as well as the moments induced into the structure by external loads (i.e., attitude control thrusters).
- (3) Minimal thermal gradients across the structure.
- (4) Ability to be displayed or erected from a high-density delivery vehicle payload.

A review of these conflicting requirements shows that the electrical requirements would seem to bar the use of some potentially good structural approaches. For example, the use of internal pressure to stabilize large compression members is unacceptable because of the danger of leakage. Material selection is limited to the aluminum alloys because of the high resistivity of the lightweight alternatives (carbon or boron filament composites, fiberglass, etc). These factors, together with the heat-dissipation requirements for large surface areas and a good view of space, suggest that a structure of large-diameter, thin-wall aluminum tubing is desirable. In the baseline configuration, 6061 aluminum alloy was selected for the bus/structure as combining good structural properties with an electrical conductivity approximately 70% that of pure aluminum. Figure 9 illustrates possible approaches to configuring the bus material into an acceptable structure and suggests the weight tradeoffs which must be performed.

The present baseline structural concept is illustrated in Fig. 10 and consists of large, triangular section compression struts built up, progressively, from small truss elements. Thermally, this concept is acceptable, as the open configuration virtually eliminates thermal gradients; it also has potential for packaging as a high-density delivery payload. Further study is needed to determine the efficiency of this type of multijoint structure when used as an element of the electrical power distribution system.

Because of the electromagnetic forces which attract similar parallel currents, all the structural cross-sections shown in Fig. 11 are in a state of hoop compression. Where parallel opposite currents occur in the configuration, notably in the mast, their mutual repelling forces may be used to good advantage. Figure 11 shows that the net outward forces acting on the exterior ring of coaxial busses may be used to "hang" the nonstructural outer busses from the structural internal busses, the outer ring being constrained only by nonconducting tension members.

The preceding paragraphs outline those factors which must be considered in the development of an optimum structural concept. The problem of resolving the conflicting power distribution thermal and structural requirements is extremely complex, and the analysis to date has served to identify the elements of the problem.

The SSPS thermal environment is shown in Fig. 12. The eclipse periods are centered about both the vernal and autumnal equinox and reach a maximum time in shadow of 72 min.

All elements of the solar collector structure, because of their open-work configuration, are essentially at the same steady-state temperature; thermal gradients across the structure are therefore minimal. However, when the SSPS enters the earth's shadow at the eclipse periods, very rapid thermal excursions occur due to the very thin material of the elements used to make up the major structural members. The curve shown in Fig. 13 represents a typical thermal excursion time-history for 0.025-cm aluminum flat sheet, in transition from sunlight to eclipse in deep space. It can be seen that the temperature drop in the first 50 sec is about 100°C assuming no thermal lag. The structural deflections associated with the spacecraft's transition from sunlight to shadow are shown at the right of the figure. One implication which can be drawn is the importance of not mixing materials with differing coefficients of expansion if a warping type of distortion is to be avoided. A satisfactory method of assessing the loading and dynamic effects of these rapid dimensional fluctuations remains to be analyzed.

One interesting concept to minimize the power distribution and structural support integration problem has been proposed by Spectrolab. By increasing the size of the silicon photovoltaic cells to where one current loop would transverse the solar array, 40 kV would be produced at one main horizontal collection bus. This approach is illustrated in Fig. 14 and would substantially reduce the number of current-carrying structural elements.

The electromagnetic field interaction between the SSPS and the earth was also considered. Fortunately, the effects of this interaction are small because of the direction of the current loops in the solar blankets as shown in Fig. 15. Each blanket segment has an associated magnetic field; however, each magnetic field is adjacent to a field of opposite polarity, resulting in the net magnetic field being extremely small.

#### Summary and Conclusions

A brief review of the SSPS concept has been presented outlining how the initial power distribution structural, and thermal environment requirements have been resolved into the present conceptual design. The SSPS electrical power distribution and structural support system contributes approximately one-third of the total orbital weight. Maximizing the orbital power-to-weight ratio has been a driving consideration and improving this ratio (as well as the important cost per KW) can be achieved by:

- (1) Integrating the power distribution and structure systems.
- (2) Selecting maximum system voltage compatible with the microwave system.
- (3) Performing weight trade studies of system distribution efficiency versus oversized solar collectors.

The factors which must be considered in the development of an optimum structural concept were identified, and the considerations leading to the selection of the triangular section compression strut network were reviewed. Additional study is required to determine the efficiency of this type of multijoint structure when used as an element of the electrical power distribution system.

One approach to substantially reduce the number of current-carrying structural elements by utilizing large-size silicon cells has been proposed by Spectrolab.

The thermal environment with its rapid temperature transients during the eclipse periods is a major problem area because:

- (1) Good electrical conductors (e.g., aluminum) are highly temperature-sensitive.
- (2) A structure configured for uniform temperature distribution (baseline using compression struts) requires indirect (complex) current paths.

Finally, orbital assembly requiring multiple joints could lead to power distribution conduction problems.

#### **Recommendations**

The problem of resolving the conflicting power distribution, thermal and structural requirements is extremely complex and the work, to date, has served to identify the elements of the problem.

Further studies to improve the power-to-weight ratios (as well as costs) should include:

- (1) Development of a microwave system compatible with higher system voltage ( $\geq 60$  kV).
- (2) Development of orbital assembly techniques to minimize the structural joints.
- (3) Large-size silicon solar cells to minimize power distribution bus lengths.
- (4) Lightweight, high-voltage insulation material.

#### **Discussion**

Q: What is the approximate power density in the microwave beam that falls on the earth and what is the approximate diameter?

A: The diameter is approximately 14 km, and we had a power density in the latest uniform beam, I think of close to  $80 \text{ mW/cm}^2$  at the center of the beam. The average over the beam was between 30 and  $40 \text{ mW/cm}^2$ .

Q: And is there any hazard to a person who walks up to the beam area if the beam wobbles slightly off of the receiving array?

A: Well, the beam cannot wander off. It automatically becomes incoherent if it goes off its target. So you get just complete scatter. You do not get a coherent beam. So you don't have a problem. If somebody stands in the way of the thing, he is going to get very, very warm. An aircraft can fly through it though without any problem. I just want to say that there is a question as to what constitutes a safe level. I understand Russia and Poland and, I believe, Czechoslovakia have standards  $1/1,000$  smaller than our nominal limits. It's a good question, I think.

Q: I'm not sure I understand the coherence. As I remember your numbers, you said you have an antenna one kilometer in diameter.

A: In orbit. On the ground your receiving antenna is 14 km in diameter. Once it starts to wander, the array itself just disintegrates, so to speak, on the ground.

Q: Am I wrong to think of the microwave beam and the array as being analogous to a flashlight which may wobble around in the space that it illuminates?

A: Not quite.

- Q: Does the return signal from the ground which is required to make the beam coherent do it?
- A: Yes.
- Q: To which part of Russia are you going to direct this beam?
- A: Unfortunately, we have always talked about Arizona.
- Q: In computing the entire industrial effort required to get this thing into space – the fuel, vehicles, etc. – what's the return time of power?
- A: It's on the order of a couple of months.
- Q: I haven't seen your paper, but I think *Spectrum* in one of its recent issues had a summary of your work that gave some costs, numbers, etc. I haven't heard you say anything this afternoon about what this costs.
- A: That's right.
- Q: My question is prompted by the fact that in Sunnyvale we are a little curious about the source of your dollar values.
- A: Well, I can defer to A. D. Little on this because they always handle the cost factoring.
- A: We have just completed a study for NASA Lewis, and the report is coming out very shortly. The main thing that we worked on was the space transportation system, and it wouldn't be apropos to this meeting as is the other work we presented.
- Q: Structural data?
- A: Yes.
- Q: What is the U. S. limit on microwave radiation?
- A: I believe its  $10 \mu\text{W}/\text{cm}^2$ .
- Q: What kind of silicon solar cell cost can you tolerate?
- A: At one time we were using numbers on the order of \$700 a kilowatt. Now we use the Stim, Ling, Currin numbers. Our costs were something like 30 cents a watt, but by the time you put concentrators and everything else on, it runs about 70 cents a watt.

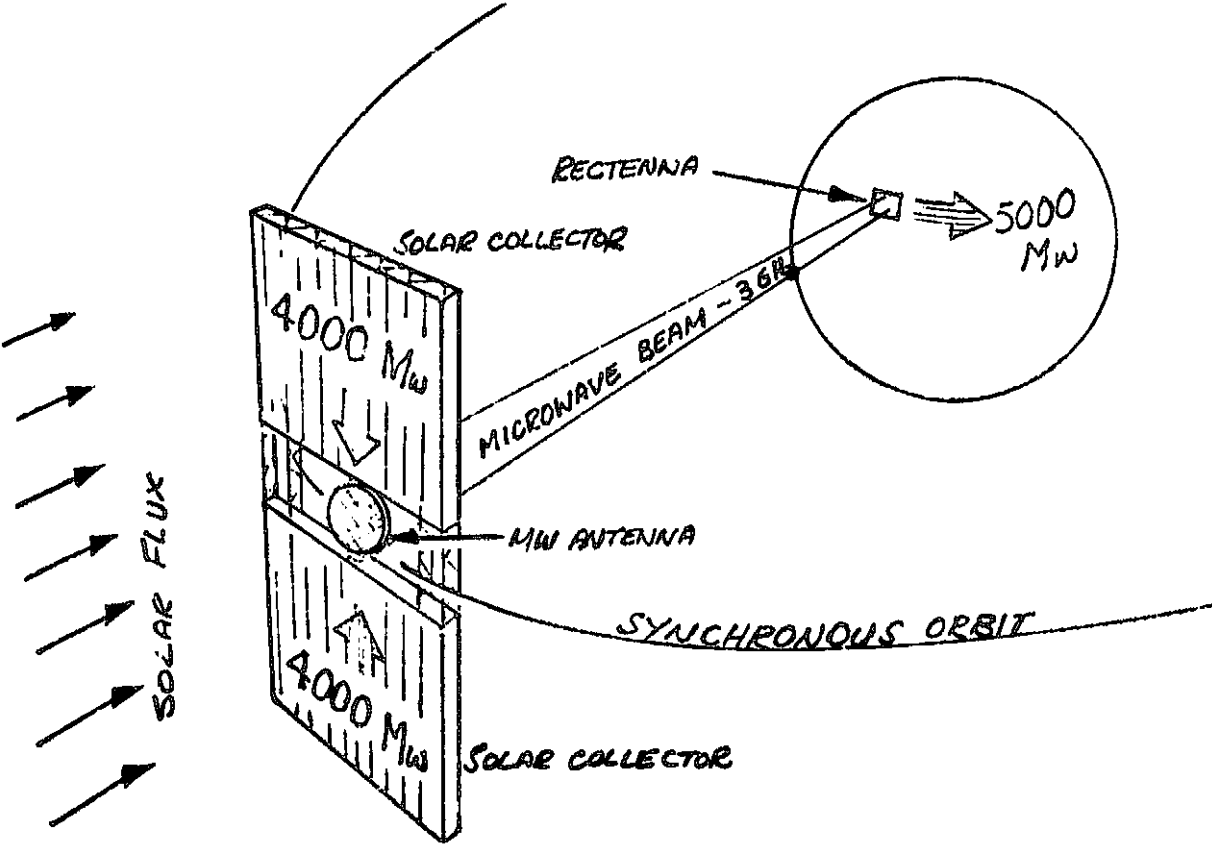


Fig. 1. SSPS Characteristics

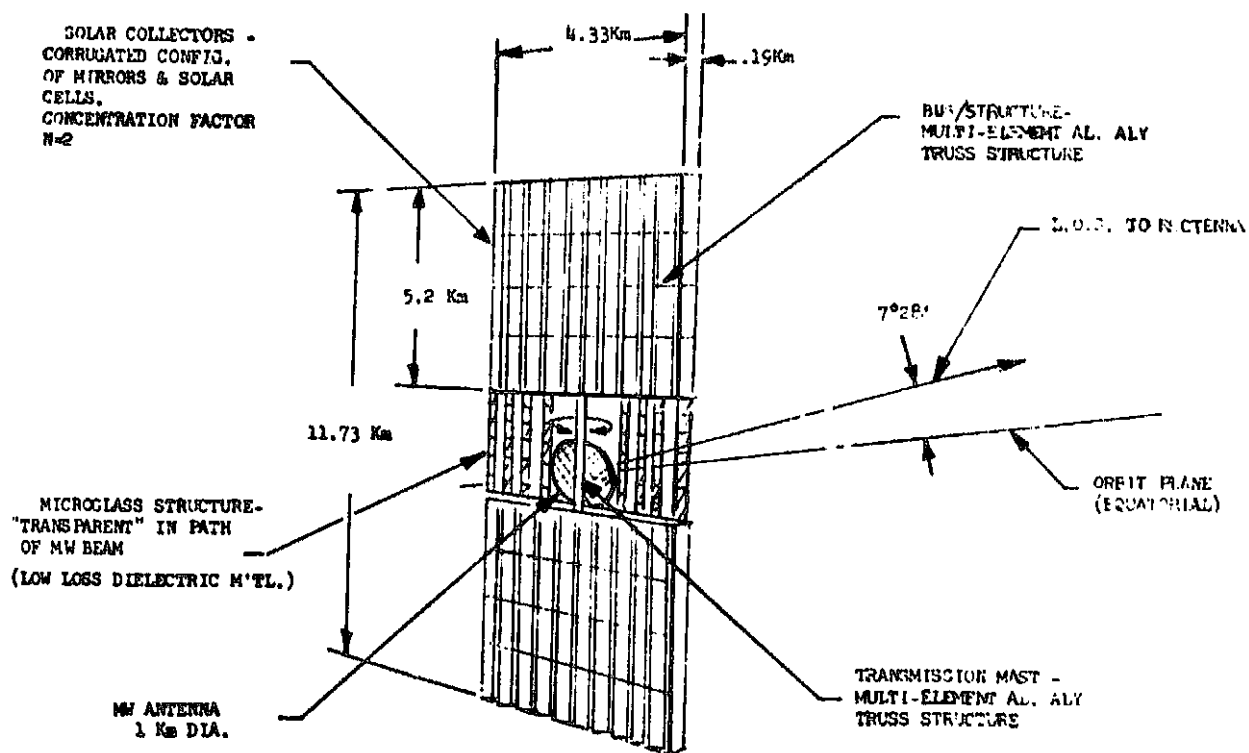


Fig. 2. Baseline SSPS Concept

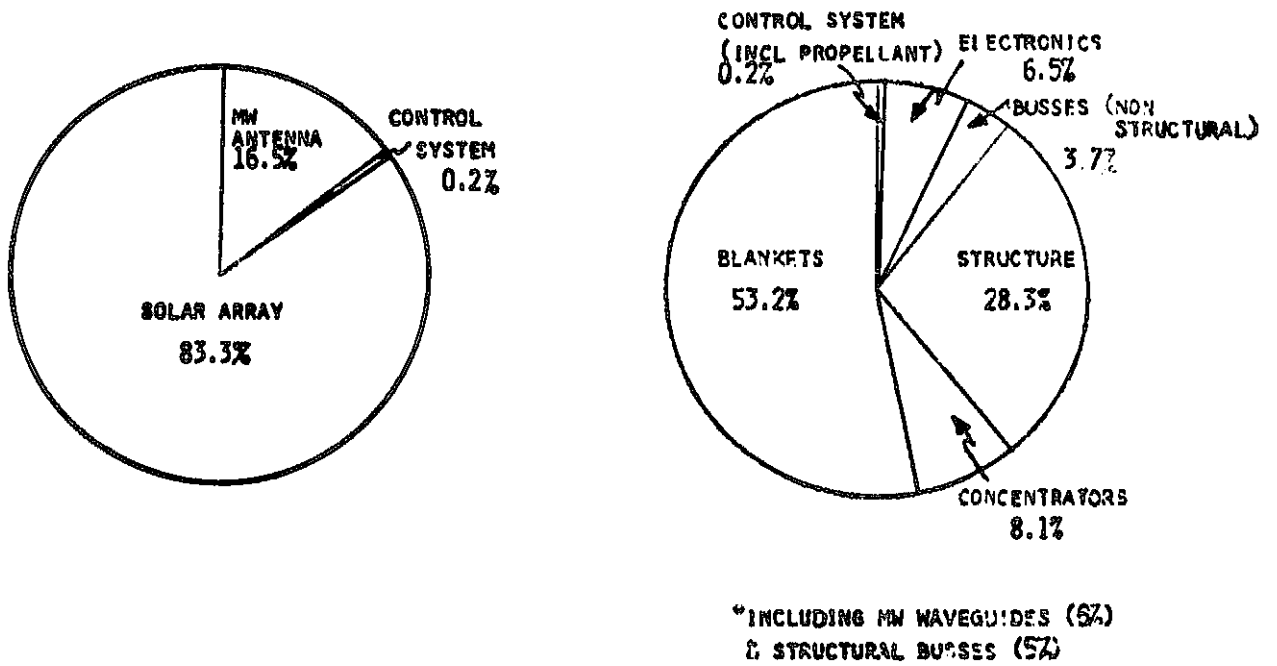


Fig. 3. SSPS Weight Breakdown

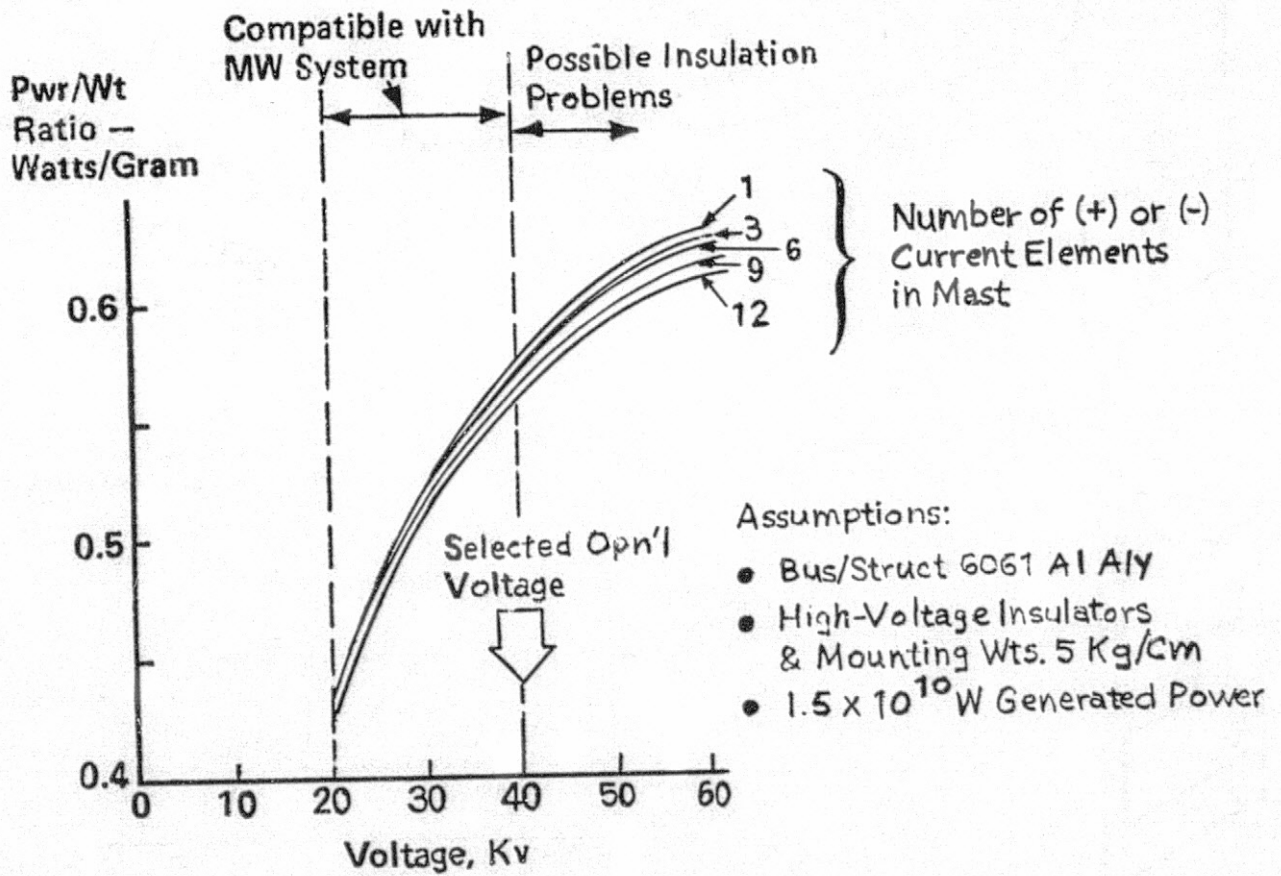


Fig. 4. Power/Weight Ratio vs System Voltage



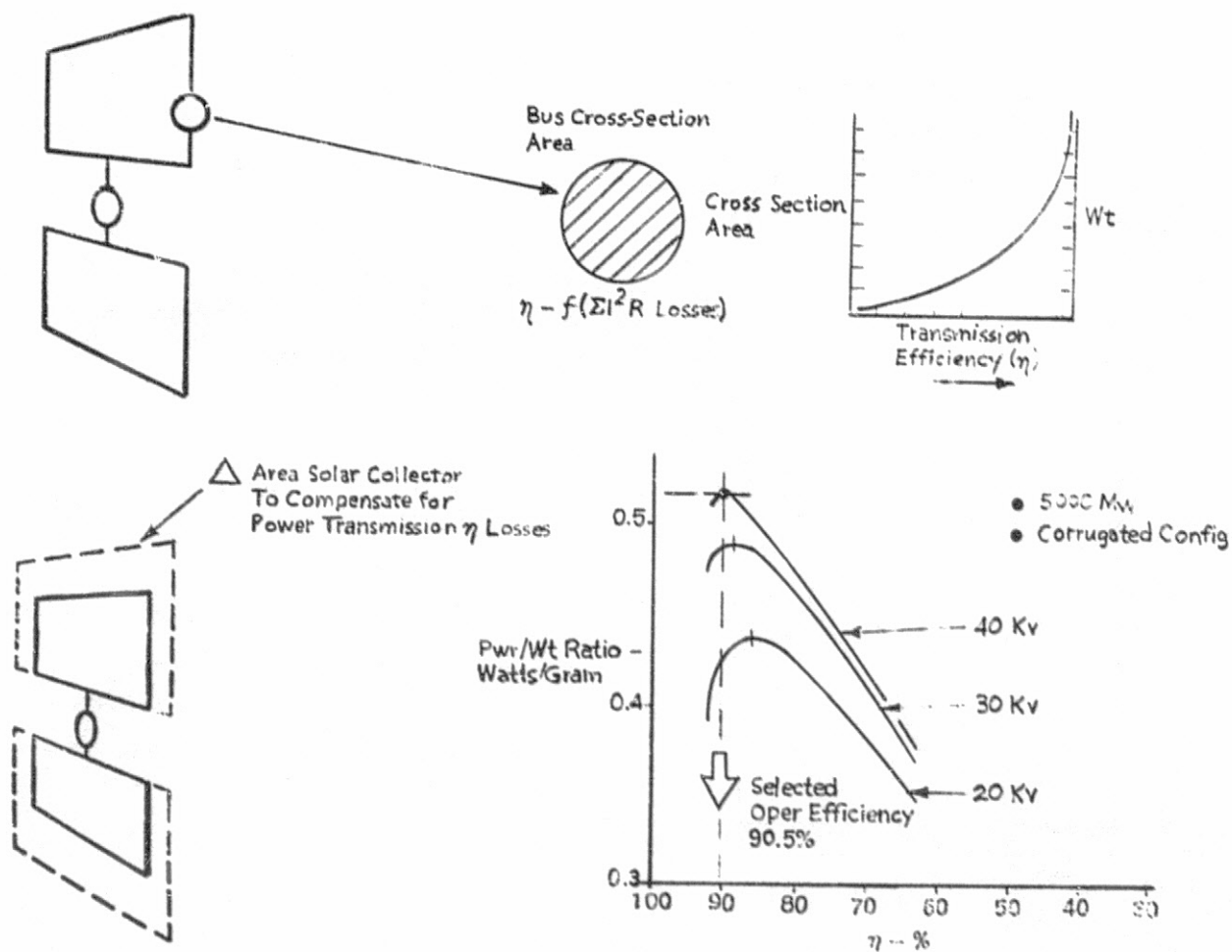


Fig. 5. Power Distribution Efficiency Analysis

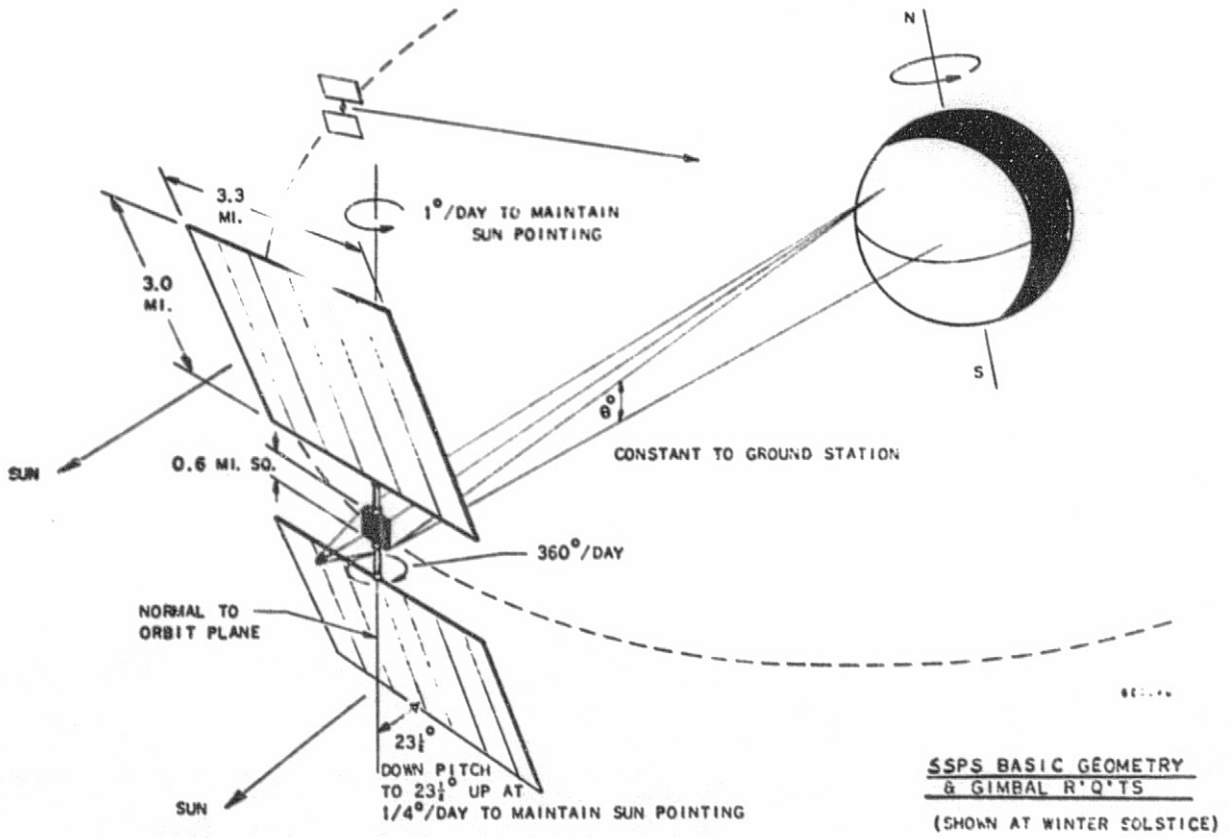
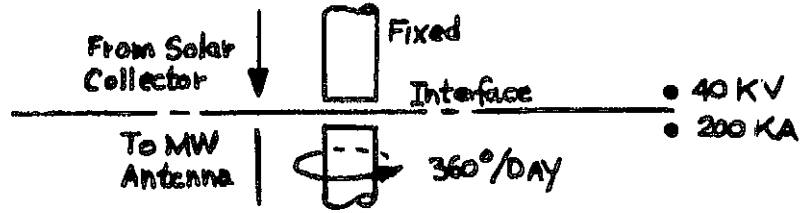


Fig. 6. SSPS Geometry



Assessment of the Options

System	State of the Art	Complexity	Reliability	Wear	Struct. Integration	Weight	Compatibility with Vacuum Environment	Select
Slip Rings & Brushes	Yes	Fair	Good	Low	Good	Moderate	Good	✓
Rolling Contact	Yes	Fair	Fair	High	Good	Moderate	Good	
Liquid Slip Rings	No	High	Unknown	Low	Fair	Moderate	Fair (outgas)	
Power Clutch with Flex Cable	Yes	High	Fair	Moderate	Good	High?	Good	
Rotary Transformer	Yes	Fair	Fair	Low	Fair	High	Good	
Arc Across Gap	Yes	Fair	Poor	High	Fair	Unknown	Poor (ionization)	
MW Across Gap	Yes	Very High	Good	Low	Poor	High	Good	

Fig. 7. Rotary Joint Power Transfer Options

● **Power Distribution System Voltage - 40 Kv**

**Because:**

- Approaches Best Power/Weight Ratio
- Good Compatibility with Solar Array System
- Fair Compatibility with Mw Transmission System
- No Forseeable Insulation Problems

● **Power Distribution System Efficiency - 90.5%**

**Because:**

- Optimum Power/Weight Ratio for Nominal 5000 Mw System

● **Rotary Joint Concept - Slip Rings & Brushes**

**Because:**

- State of the Art
- Good Wear Properties
- Technical Risk - Low
- Compatible with Structure
- Alternatives Unlikely to Improve on Performance or Cost

**An Observation**

- **Higher Voltage Distribution Systems (60-80 Kv) Should Be Further Examined**

Fig. 8. Power Distribution Characteristics Summary

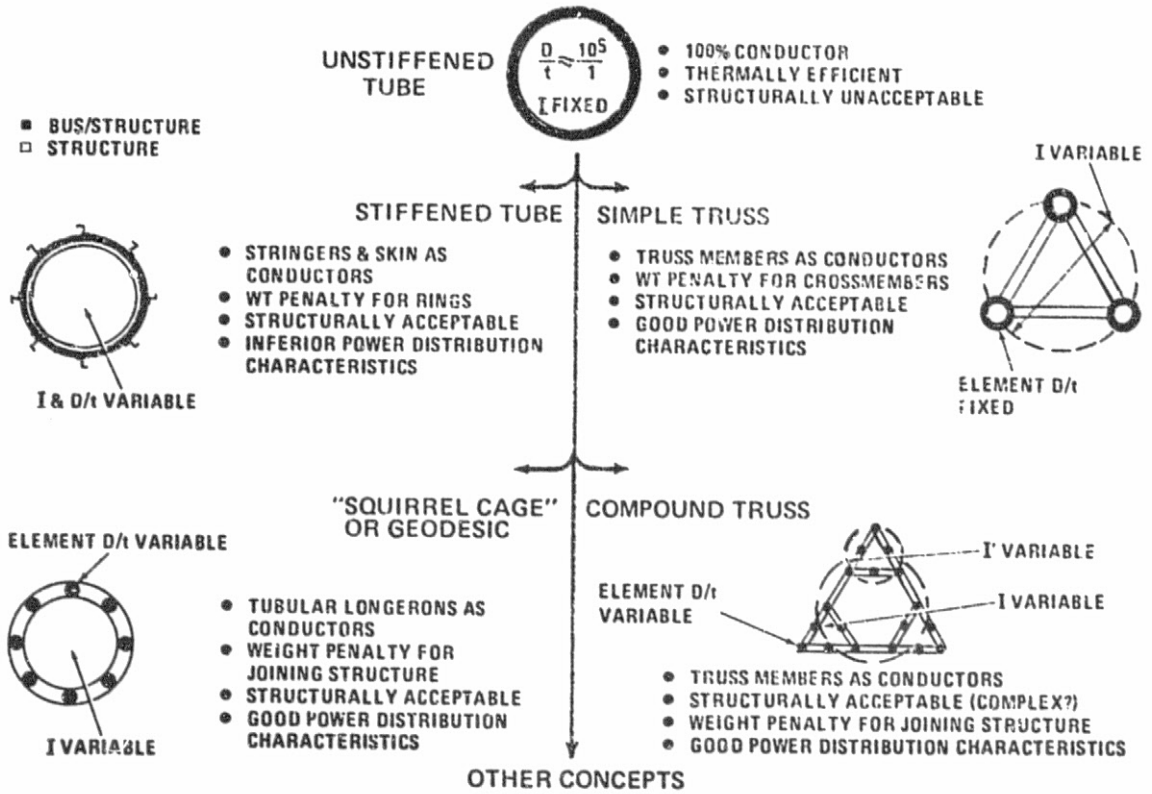


Fig. 9. Bus/Structure Optimization Trade-Offs

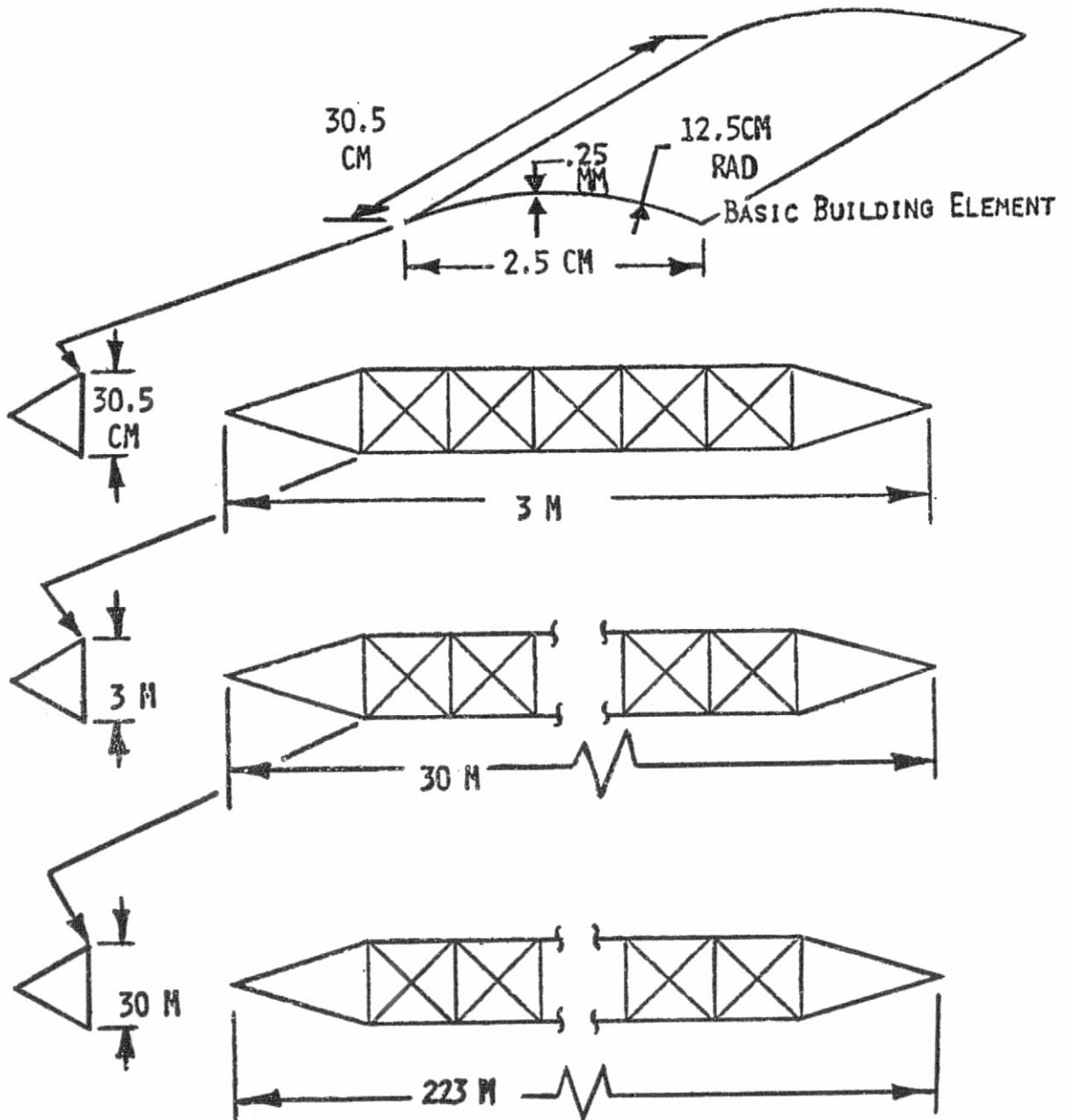


Fig. 10. Construction of Compression Strut

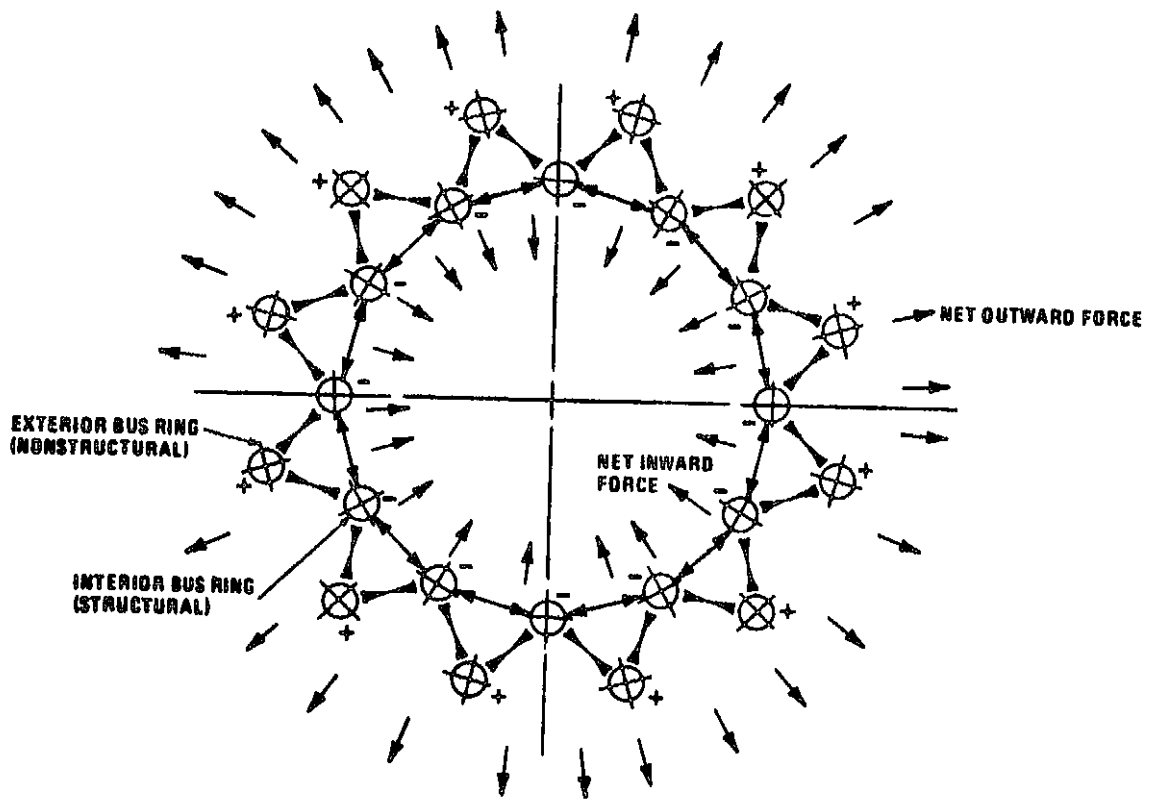


Fig. 11. Coaxial Bus/Mast Cross-Section

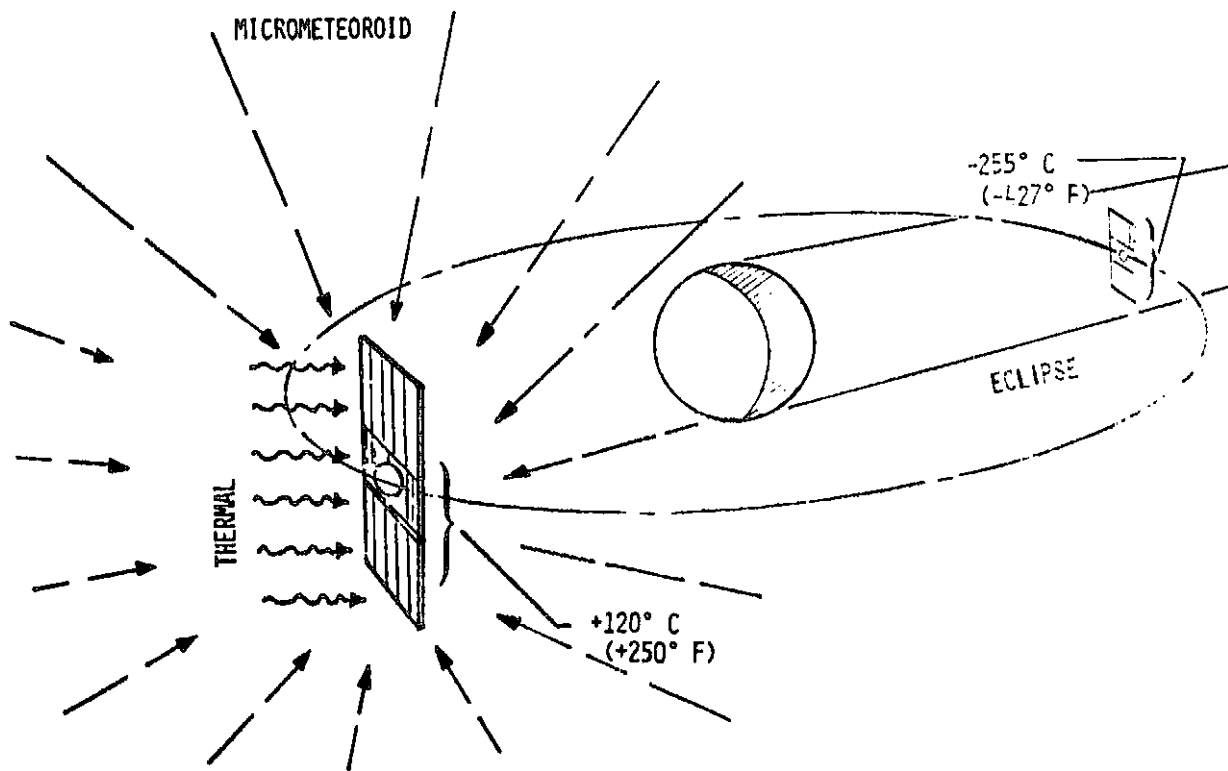


Fig. 12. SSPS Environment



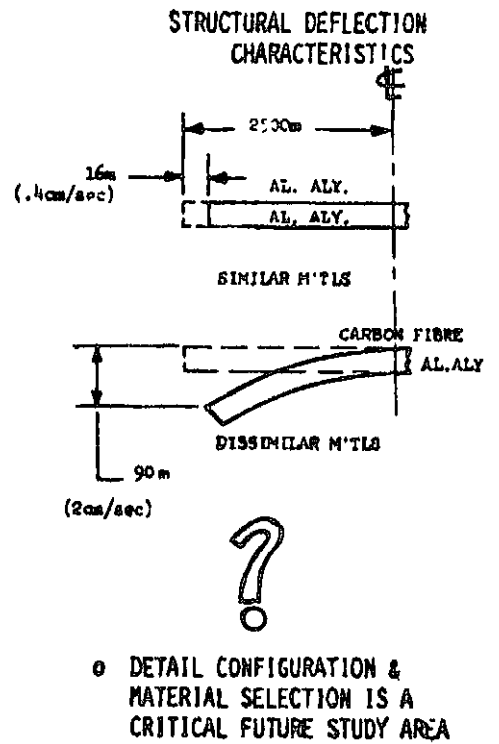
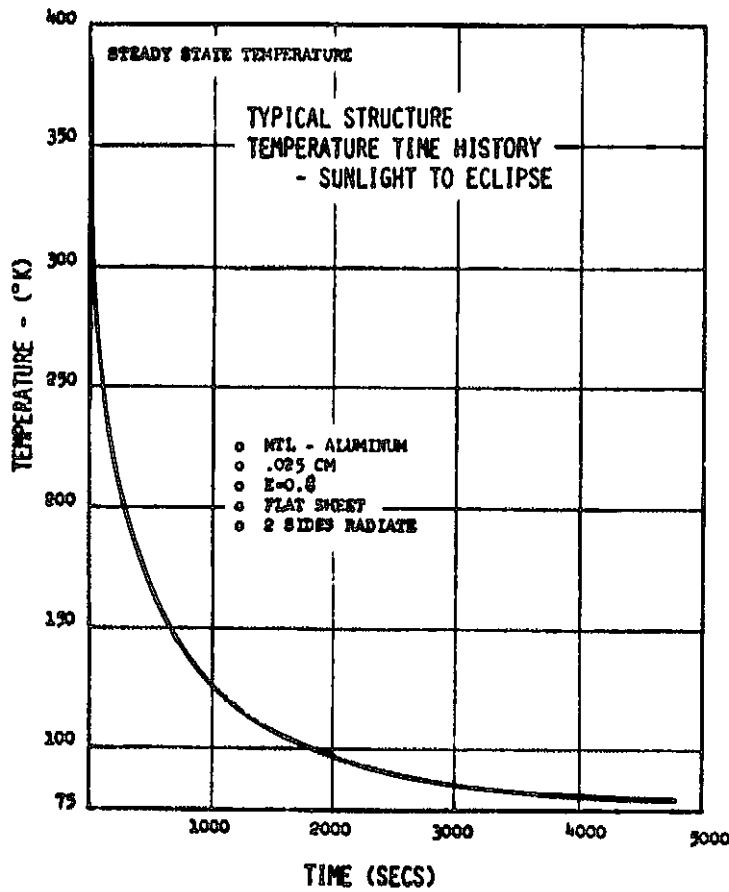


Fig. 13. Thermal Environment Implications

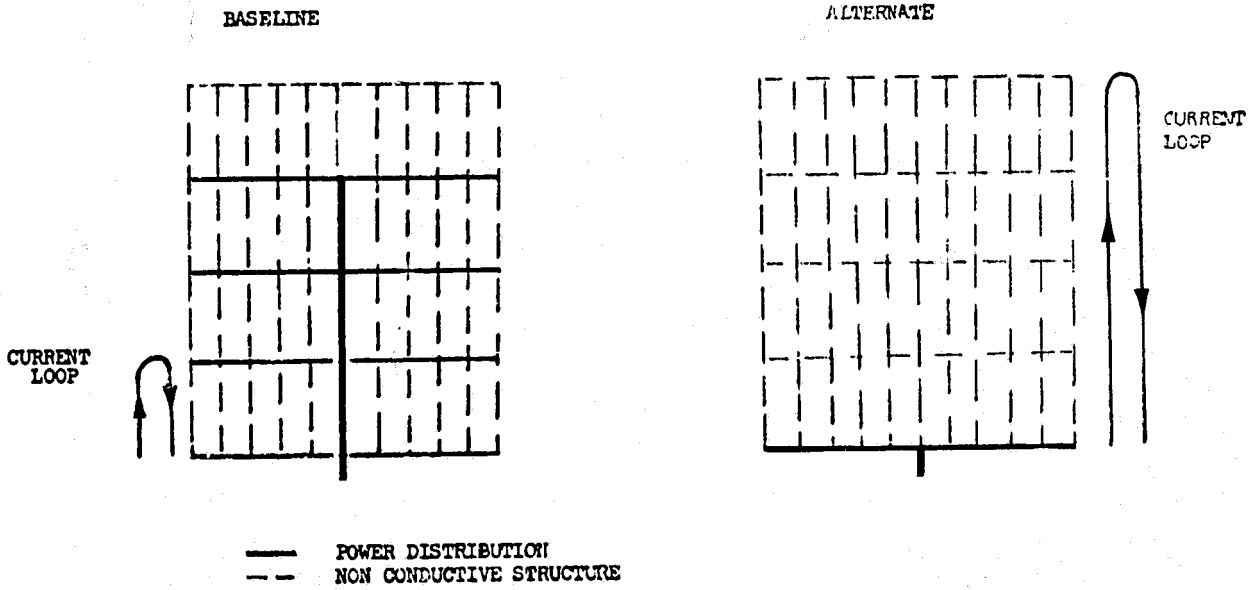
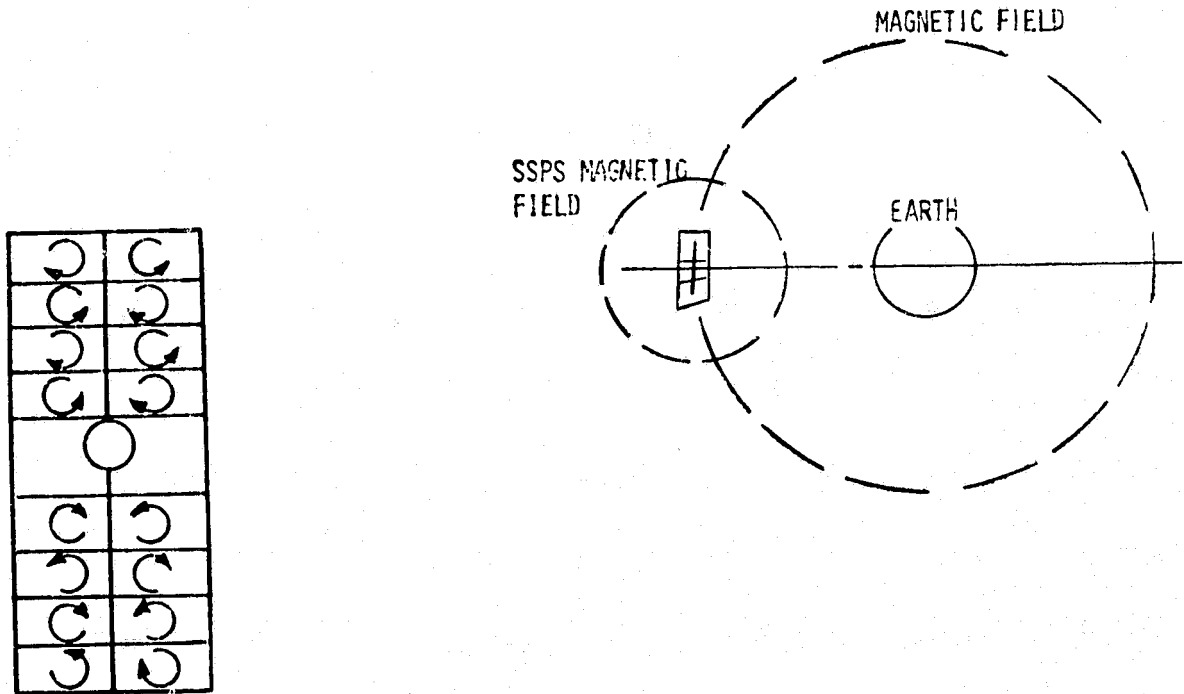


Fig. 14. Spectrolab Concept



INTERNAL CURRENT LOOPS ARE SELF BALANCING  
 NET MAGNETIC TORQUE  $< 10^{-5}$  LB-FT

Fig. 15. Electro-Magnetic Field Interaction

## PHOTOVOLTAIC TERRESTRIAL APPLICATIONS

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### Presentation Summary

The NASA Lewis Research Center has been involved in photovoltaic research and development work since 1961. The work was directed to space applications and primarily involved thin-film CdS-Cu<sub>2</sub>S solar cells. In 1971 the effort was directed exclusively to silicon solar arrays with the objective of increasing efficiency and lowering cost. Since the space market for solar cells has been relatively limited, manufacturers have had no incentive to seek lower cell cost through approaches such as production automation. We felt that significant cost reductions could be realized only if solar cell applications, in particular terrestrial, were greatly expanded. Our efforts to identify and to aid in the development of terrestrial applications of solar cell systems are displayed in Table I. The first task shown includes a demonstration solar cell powered weather station installed last year at the Cleveland Coast Guard Station on Lake Erie. Another project is the design, fabrication, and installation of solar cell arrays to power Remote Atmospheric Monitoring Observation Stations (RAMOS) for use by NOAA. One solar powered system has just been installed in Sterling, Virginia. Others will be set up next month at Mammoth Mountain, California and next year somewhere in Alaska.

The objective of the second task is to search out, list, and evaluate terrestrial applications of solar cells that could be marketed during the next 5 years. Finally, designs are to be provided for two such applications. The final report on this contract should be distributed within the next 60 days.

In the last two programs, contracts have recently been awarded to define the necessary technology, production approaches, and costs for producing low-cost silicon cells and arrays for large-scale generation of electric power to meet national needs 30 to 50 years hence.

Table II is a partial list of photovoltaic terrestrial applications in use or in the planning stage. A brief description of each area is included in the table. It is worth noting that even at today's prices of \$25 to \$50 per watt, photovoltaics systems are in some demand. Results of the present studies indicate that within the next five years the price of solar cells should be reduced to \$5 per watt. Many applications that are now in the feasibility demonstration phases and others, as yet unrecognized, will then become cost competitive with more conventional power generation systems.

Applications for solar cell power systems are growing. We are yet several decades removed from the large-scale generation of electricity from solar arrays. However, as we move toward that possibility we will uncover, to our benefit, many smaller, but quite significant, uses for photovoltaic power.

### Discussion

Q: What are the watts and costs?

A: One of these submodules puts out about one watt and costs about \$40.00 a watt. That includes solar cells, which we were able to purchase at about \$15.00 a watt and also the labor that we used in the laboratory. The labor certainly wasn't optimized.

Q: Can you elaborate on the FEP coating?

- A: FEP is fluorinated ethylene propylene. There are two 5-mil films of FEP above the interconnected solar cells. The cells in this case are interconnected by welding (parallel-gap welding), and the films are heat and pressure laminated to the cells.
- Q: What are the dimensions of that module?
- A: Three cells by eight cells. Each cell is 2 cm by 2 cm to give a rough idea. I don't know the exact dimensions.
- Q: How many days of energy storage do you need in the Cleveland area through the winter months?
- A: Lots! I don't know how much.
- Q: You haven't gone through the winter yet?
- A: No. We have some systems on our roof with batteries and so on. We think we need about a minimum of ten days' storage to operate without the array. We generally put in more storage than that, because after ten days there may not be full sunshine to charge the array.
- Q: Do you plan to take performance data on the array while it is getting the weather information?
- A: Yes, including insolation data if we can, power output, and so on.
- Q: Is there degradation data on the FEP?
- A: Well we have had some FEP up on the roof -- a module like this -- for two years I believe. We see nothing -- no effect on it at all. DuPont states that they have had FEP in Florida sunshine for seven years with no noticeable degradation.
- Q: Do these surfaces need any kind of cleaning maintenance in a suburban or urban area?
- A: No, we have a pretty dirty rooftop and we have done nothing to the arrays at all. The FEP teflon is a pretty slippery surface, and the arrays stay fairly clean. We have also used plexiglass-covered arrays on the roof. Surprisingly, they also stayed relatively clean.
- Q: Is it better than glass?
- A: It appears that way, yes. The modules are mounted at about a 45° angle, so that makes a difference, too.
- Q: Then you did not find any degradation of the entire module, including the silicon cells?
- A: That's right.
- Q: How are they mounted to the aluminum substrate?
- A: The FEP is used as the adhesive also, and the same FEP is all heat laminated in one package.

Table I. NASA-LeRC Photovoltaic Terrestrial Programs

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<b>OBJECTIVE</b>	
Reduce costs of solar arrays	
<b>APPROACH</b>	
Develop very low cost cell and array fabrication methods. Encourage terrestrial market for arrays.	
<b>PROGRAMS IN PROGRESS</b>	
Solar Cell Powered Weather Station	In-House
Terrestrial Applications of Solar Cell Powered Systems	Heliotek, \$39K
Low Cost Silicon Solar Cell Arrays	Spectrolab, \$37K
Low Cost Silicon Solar Cell Arrays	Centralab, \$32K

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Table II. Photovoltaic Terrestrial Applications

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<b>Communications</b>	Remote or portable microwave relays, telephone systems or telephone/radio repeaters
<b>Meteorology and Hydrology</b>	Weather monitoring and data gathering, automatic systems for flood warning, snow-level, seismic detectors
<b>Marine Navigation Aids</b>	Lighthouses, marker buoys
<b>Offshore Platforms</b>	Primary or emergency power
<b>Environmental</b>	Water quality sensors
<b>Highway Safety</b>	Emergency telephones
<b>Forestry</b>	Fire warning, fire control

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## EVALUATION OF SOLAR CELL COST PREDICTIONS

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### Presentation Summary

The purpose of this paper is to examine the feasibility of the initial goal of the National Science Foundation photovoltaic conversion program, i.e., to reduce solar cell production costs by a factor of 10 from the present cost of approximately \$50 per watt. Also reviewed is the relationship between present costs and the long-term goal of \$0.50 per watt required to insure that photovoltaics become a competitive alternative energy source.

The major source of information for this paper is the paper, "Feasibility of Low Cost Silicon Solar Cells," by Currin, Ling, Ralph, Smith, and Stirn, which was presented at the 1972 Photovoltaics Specialists Conference. In addition, other data from the space program is used along with new developments which have occurred since 1972.

Table I represents cost summaries in dollars per watt obtained from the sources noted above. Column 2 represents 1972 production costs based on conventional production processes. The significant factor is the large cost variation between solar cell blanks and completed solar cells. This discrepancy will be discussed later as it directly affects the capability for meeting the short-term photovoltaic program goals.

Column 3 in the table indicates the potential cost impact of the new, higher efficiency violet solar cells. Costs are predicated on a projected 20 percent AMI efficiency. These figures assume that the solar cell production costs do not increase significantly as a result of more complex processing requirements.

Column 4 represents an estimate of future minimum costs based on extensions of present technology (including violet cells) and assuming high rate production. Close to an order of magnitude improvement in cell blank costs is indicated as compared to 1972 technology. However, if there were not a comparable improvement in completed solar cell costs, the overall cost effect would be negligible.

Column 5 represents cost data which certain cell manufacturers have indicated is possible within the next few years. Based on the cost data previously described, it can be seen that either a significant cost reduction in solar cell production costs is anticipated, or the use of solar array concentration is being planned.

Column 6 indicates projected costs based on continuous silicon ribbon growth techniques. It is evident that advanced processing technology of this sort is required to approach the overall long-term system requirement of \$0.50 per watt.

In summary, the critical problem area related to the short-term cost goal of \$5.00 per watt for solar cells is the large cost factor associated with the processing of solar cell blanks to completed solar cells. The following factors have been identified as reasons for the relatively high cost for solar cells:

- (1) Nonstandard specification requirements.
- (2) Rigid space quality control and cosmetic requirements.
- (3) Complex and nonautomated production processes.
- (4) Low and varying production requirements.

It is difficult to assume that any changes can be made with respect to factor (4) in the near future. The imposition of standardization and the relaxation of quality and cosmetic requirements, as covered by factors (1) and (2) may

result in some cost savings due to reduced scrap rates. However, past estimates from cell vendors have indicated that cost savings in the order of only 10 percent - 15 percent could be expected from these factors.

It is clear that factor (3) is most critical with respect to potential cost benefits. It is doubtful that significant cost reductions can be made in the near future unless production processes could be simplified as a function of reduced efficiency, quality requirements, and cell geometry designed to reduce scrap rates.

It thus appears that simplifications will be required in the processes used in converting solar cell blanks to completed solar cells and/or the use of concentration schemes will be required to reduce present day solar cell costs by an order of magnitude in the near future.

### Discussion

- C: The numbers you have given from the paper by Currin, et al., assumed a process where you get essentially 90 to 100 percent conversion from the poly to single crystal.
- A: Thank you.
- Q: How do you get that 20 dollars a watt for a space-type cell?
- A: That corresponds to like \$4.00 for a 2- by 2-cm cell.
- C: It should be higher than that. You haven't paid \$4.00 for a two by two for over two and one half years.
- C: One thing is that you buy your solar cells with a 43-page specification. It seems to get about two pages longer each year. You buy them made to your customs and specifications; so I think that there are good reasons why it is so expensive.
- A: The only comment I have to make about that is not really in rebuttal but that in other meetings when we have had discussions about how much would it save in space programs to reduce the spec, the numbers I heard were something like ten or fifteen percent. The numbers were not that significant, if you cut back on the spec and accept blemishes, things of this sort.
- C: The cost of being in business to build those cells for you when you want them is a certain fixed cost of business. I think that's the problem.
- A: I realize this.
- Q: In a nutshell, what are the implications of the figures that you have provided?
- A: I'm not sure that they have any implications other than that I'd like to buy a \$5.00 a watt cell, and I am going to try to do that in a short period of time. Then I'm going to question the reason why we specify to such a degree so as to make us pay \$40 a watt for a space cell. That could be an implication. The other implication I wanted to make is that now there are lots of numbers about dollars per watt, and you have got to make sure that we're talking about a cell that was made for you, as opposed to a cell that isn't worth anything because it was rejected by some other customer.
- C: I don't think you have ever bought a 20-square-centimeter cell for your spacecraft.
- A: That is right.
- C: There's a large difference in cost. As was pointed out earlier, not only is solar cell technology a moving target, but so is crystal growing.

Table I. Cost Estimates and Projections

Type Cells	Dollars per Peak Watt					Requirement
	1972 Technology	Violet Cells	Minimum Costs	Terrestrial Cells	EFG Cells	
Polycrystalline Silicon	0.35	0.18	0.10			
Single-Crystalline Silicon	0.80	0.40	0.18			
Solar Cell Blanks	3.20	1.60	0.40		0.25	
Completed Solar Cells	60.00- 80.00	40.00		5.00	0.37	
Solar Arrays	120.00-160.00	80.00		10.00		
Solar Power Systems				20.00		0.50
Cell Efficiency	10%	20%	20%		10%	
Cell Thickness	10 mils	10 mils	10 mils		4 mils	



**SESSION IV**  
**CdS/Cu<sub>2</sub>S THIN FILM CELLS**

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#### **SESSION IV. CdS/Cu<sub>2</sub>S THIN FILM CELLS**

**SOLAR ENERGY PROGRAM AT UNIVERSITY OF DELAWARE—K. W. Böer**

**ELECTRIC POWER GENERATION THROUGH THIN FILM PHOTOVOLTAIC CELLS—  
T. P. Brody and F. A. Shirland**

**SUMMARY OF THE NASA—LEWIS CdS SOLAR CELL PROGRAM—H. W. Brandhorst**

**DEFECT STUDIES IN SOLAR CELL MATERIALS—L. L. Kazmerski**

**DEVELOPMENT OF LOW COST SOLAR CELLS—J. F. Jordan**

## SOLAR ENERGY PROGRAM AT UNIVERSITY OF DELAWARE

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**Presentation Summary**

The program at the Institute of Energy Conversion at the University of Delaware embraces research on both photovoltaic cells and systems. Diagnostic tools such as SEM, TEM, Auger spectroscopy, electron diffraction and Moire patterns have been used extensively to study the physical properties of the solar cell layers. Dr. I. Greenfield has already reported on some of the results of these studies. Here we report on some of the electrical characteristics of the cells.

I-V curves for 3" X 3" CdS/Cu<sub>2</sub>S cells in both dark and light are shown in Fig. 1. From these curves the series and shunt resistances are determined. Further analyses shown in Figs. 2, 3, and 4 enable us to obtain the diode characteristics of the junction. Fill factors of 70-76 percent are found and efficiencies up to 5.3 percent.

Since one of the main goals of our research is to find a means of stabilizing the cells and obtaining better reproducibility, we are investigating how production changes affect the cell parameters. The spacing and width of the grid lines have been varied to change both the series resistance and the short-circuit current. Figure 5 shows I-V curves corresponding to 60 X 10 lines per inch (1 pi), 10 X 10 lpi, and 5 X 5 lpi with grid thickness 0.00045 inches and width 0.001 inches. The gain in efficiency exceeds that which would be expected from simply having a greater active area. It may be that the contacts act as recombination centers.

Large and small cells have been studied, the large cells had series resistance problems, while the small cells didn't. Using thicker wires relieved the series resistance problem. Cell efficiencies of 4-5 percent with 7 X 7 lpi are possible and much cheaper than the Clevite cells, which had 60 X 10 lpi.

Another process control investigation involves the sheet resistance of the Cu<sub>2</sub>S layer (Ref. 1). The sheet resistance of 3" X 3" cells is shown in Figs. 6 and 7. The uniformity of the sheet resistance of the finished cell is determined by the cleaning procedure used on the copper substrate. The sheet resistance can also be used to study the basic properties of the cell. Figure 8 shows that the light-generated current is proportional to the square root of the sheet resistance,  $I_L \propto (\rho/t)^{1/2}$ . One can derive such a relationship if one assumes that the thickness  $t$  of the layer is uniform and greater than the diffusion length  $L_n$ . One has

$$I_L \propto GL_n$$

where  $G$  is the electron generation rate due to illumination. For  $L_n$  one has

$$L_n = (D_n \tau_n)^{1/2}$$

where  $\tau$  is the electron recombination lifetime and  $D_n$  the diffusion constant. Using the relation

$$\tau_n = \frac{1}{\sigma_r V_{th} p} \propto \frac{1}{p}$$

where  $\sigma_r$  is the recombination cross-section,  $V_{th}$  the thermal velocity, and  $p$  the hole concentration in the p-type layer. The resistivity  $\rho$  is given by

$$\rho \equiv \frac{1}{\sigma} = \frac{1}{ne\mu_n + pe\mu_p}$$

For  $\mu_p$  constant, one has  $\rho \propto 1/p$ . We thus obtain the relation

$$I_L \propto (\rho/t)^{1/2}$$

Solar cells have been deployed on the roof of the Institute and in solar panels on Solar One, the demonstration solar house at the University of Delaware. Life-testing studies over a period of 36 weeks under conditions in which the temperature at noon reached as high as 80°C indicate that in this highly degrading environment a lifetime of eight years for 50 percent degradation in power output. Accelerated life testing using 24 hr/day illumination at different temperatures and gas ambients yield an extrapolated lifetime of five years for a nitrogen ambient at 50°C. If this is corrected for the average hours of sunlight that a deployed cell would experience in a terrestrial application, then a lifetime in excess of 20 years can be expected. A further indication of longer lifetimes is that when the cells are left in darkness and at lower temperatures for several days, a marked recovery of output is observed on subsequent testing. The five-year lifetime at 50°C correlates (Ref. 2) well with the diffusion of copper in CdS. It may be that part of the degradation mechanism is related to diffusion of copper into CdS.

The solar panels on the roof of Solar One are kept below 150°F and are flushed with nitrogen gas. No degradation has been noted on the house panels. The heat from the roof of the house is used to charge a heat reservoir for thermal heating or cooling of the house.

### References

1. Hadley, H., and Nelson, W., *Preliminary Cu<sub>x</sub>S Sheet Resistance on Thin-Film Cu<sub>x</sub>S/CdS Solar Cells*, NSF/RANN/SE/GI34872/TR73/13.
2. Böer, K. W., Freedman, N., Hadley, H., Nelson, W., Selcuk, K., Birchenall, C. E., Olson, J., and Partain, L., *Flat Plate Collectors with CdS Solar Cells and First Indications of Feasibility for Their Large Scale Use*, NSF/RANN/SE/GI34872/TR73/1.

### Discussion

- Q: Can you tell me the resistivity of the layers?
- A: The resistivity of the copper sulphide layers? This varies over a wide range depending on how the layers are made. It is quite sensitive to the stoichiometry. With slight variations of temperatures and the way these are made, the resistivity of the copper sulphide can vary easily over two or three orders of magnitude.
- Q: From where to where?
- A: That's a good question. I should look this up.
- Q: What about the cadmium sulphide?
- A: The cadmium sulphide? One ohm-centimeter.
- Q: What contact material did you use with the copper sulphide?
- A: Gold and copper.

**Q:** I know you have a unique system here that blows air over the backside. I am wondering if you have a chance to study any of the effects of when the air shuts off. For example, does that raise the temperature of the cell?

**A:** Yes. While we have used air here for the specific reason of having a fail-safe situation, we don't necessarily want to say that the air is the best heat transport fluid. But what we have are weight-assisted louvers in the basement and the top of the attic, so that we have a chimney effect. The backsides have fins so that we have accelerated cooling, and the maximum temperature which we have measured is 190°F. This is too high. We need some additional finning to stay below that temperature, but it is our intent to keep the cells cooled less than this.

**Q:** But in a normal house, you know, when you turn a fan on and off and what happens is ---

**A:** No, that is a separate fan.

**Q:** What activation energy could you derive from the life test versus temperature data, and how does that compare with the diffusion activation energy of copper?

**A:** The activation energies are similar, but not identical. Now, to put a straight line through three points is, of course, dangerous, and you have seen a number of curves which go in all directions. I have used the steepest curve. Of course, the reason for this is that the other curves which are not quite as steep were obtained by using gases which contain a little oxygen (for instance, argon), so we thought that additional processes (photochemical processes) take place. But the slopes are not identical. The numbers come out somewhat similar to each other, but I think we have to weigh the results much more carefully before we can make a definite statement.

**Q:** Where does the action take place? In the copper sulphide or in the cadmium sulphide?

**A:** That's a matter of definition. We have two things. One is the spread of the quasi-Fermi levels, and we have the feeling that both cadmium sulphide and copper sulphide are involved there. The electrons, however, seem to come predominantly from the copper sulphide. That is, it is electrons that are transported and that are contributing to the actual short-circuit current, much less than holes.

**Q:** What is the effect of moisture on these cells?

**A:** Terrible! We have cadmium sulphide cells on the roof of the Institute, but during the winter time, in January or February, we found condensation inside. So there must have been cracks through which humid air was admitted into the system. As a result of this, these curves dropped very rapidly as soon as humidity was involved. You have to realize that this is a series of 400 cells. The bottom eight cells were the first ones to degrade very rapidly, determining the slope of this curve. We have taken some of these cells apart and found that not all cells degrade very rapidly. Some degrade very rapidly as soon as humidity is introduced.

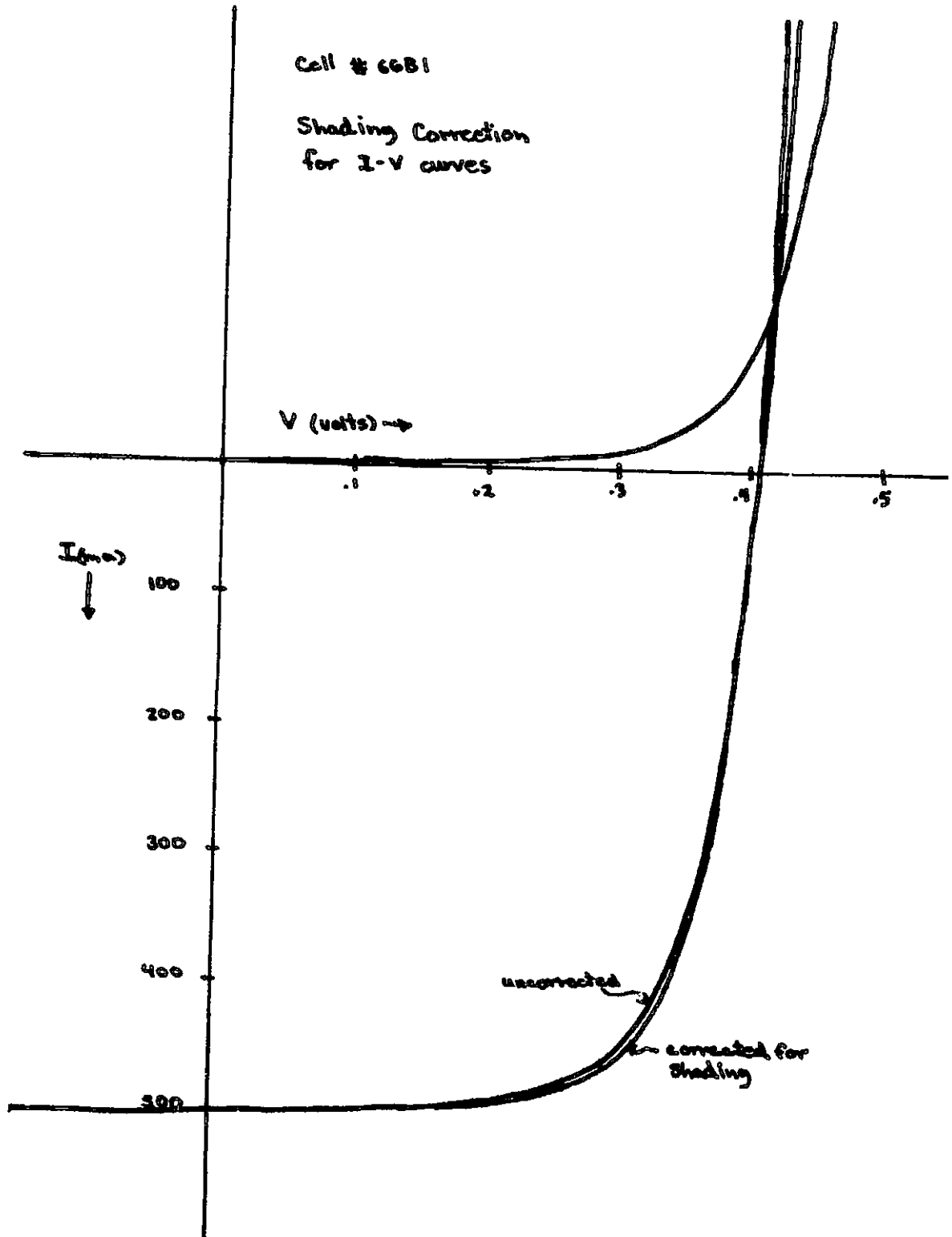


Fig. 1. I-V Characteristics in Dark and Under Illumination

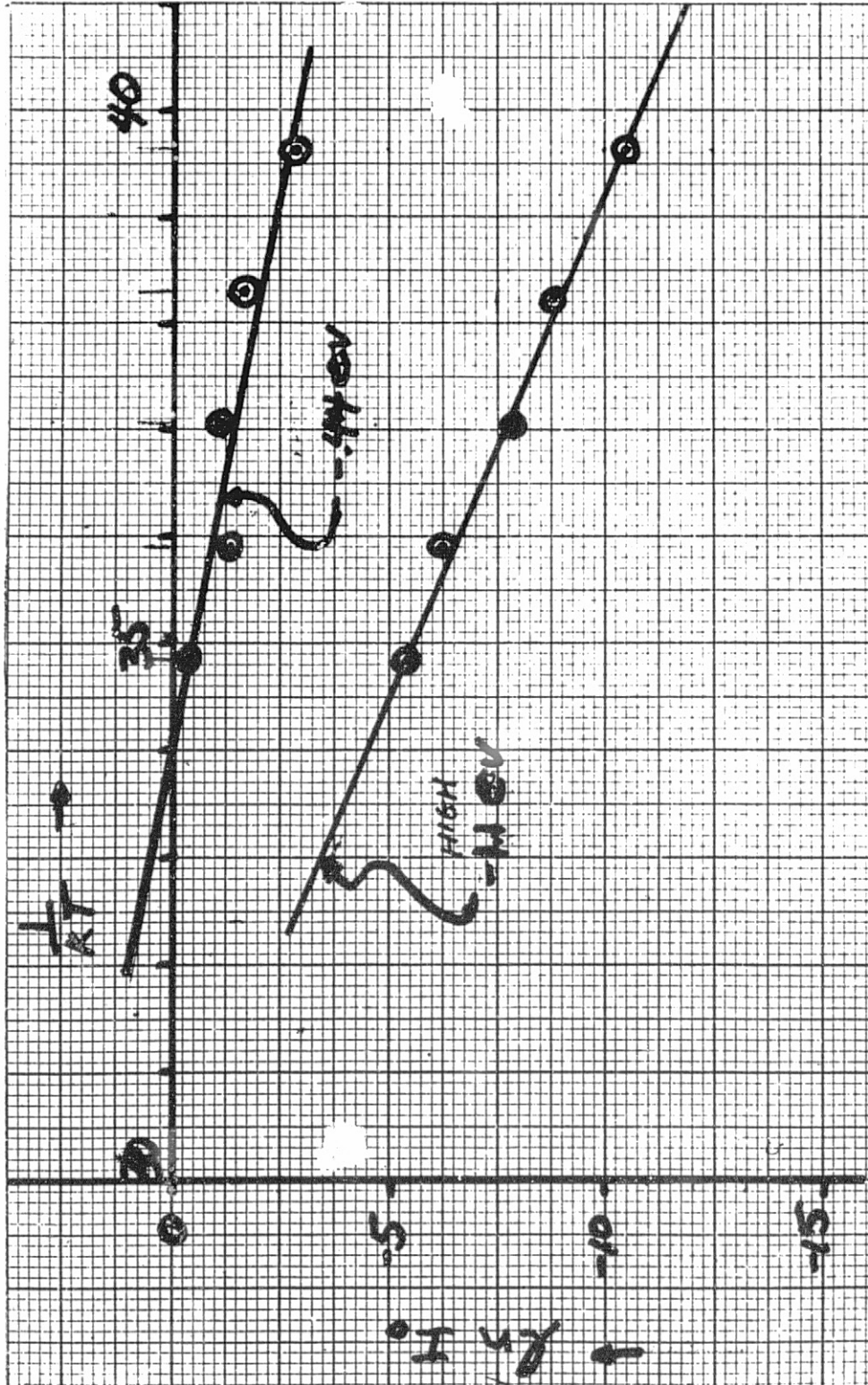


Fig. 2.  $\ln I_0$  vs  $1/kT$

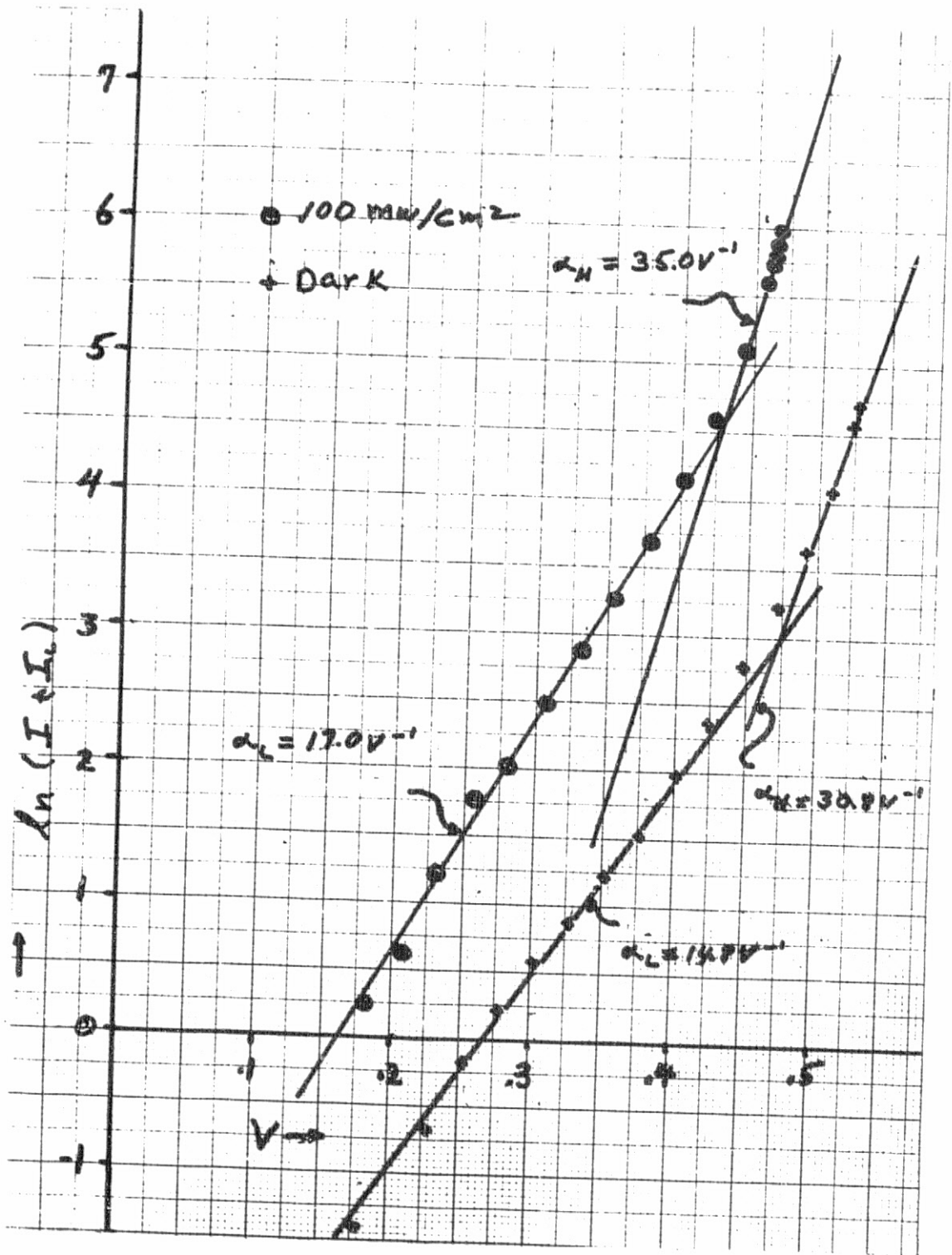


Fig. 3.  $\ln(I + I_L)$  vs  $V$



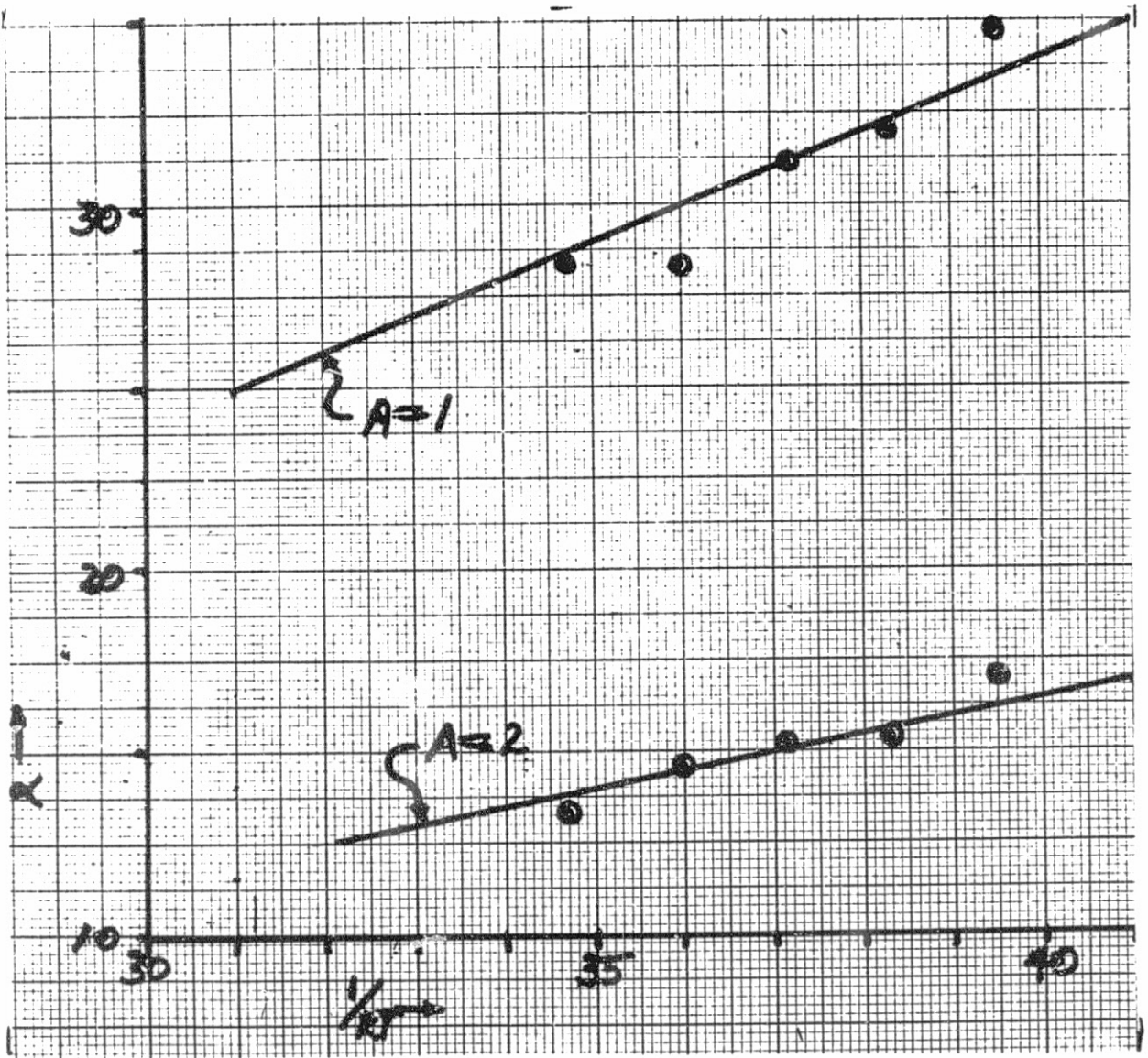


Fig. 4.  $\alpha$  vs  $1/kT$

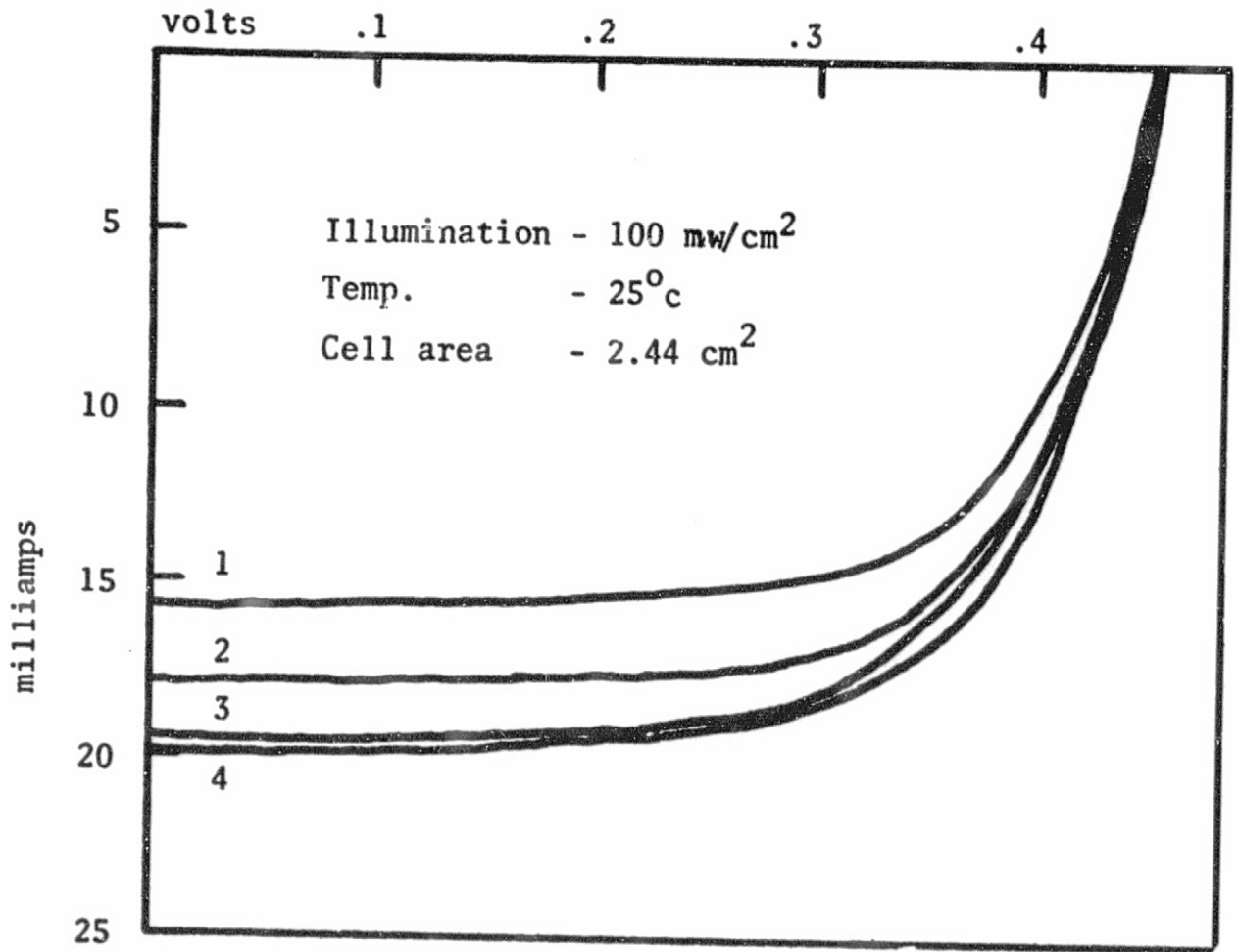


Fig. 5. I-V Curves for Various Grid Spacings



Fig. 6. Old Cleaning Procedure: Alconox Scrub, Water Rinse, HNO<sub>3</sub> Etch

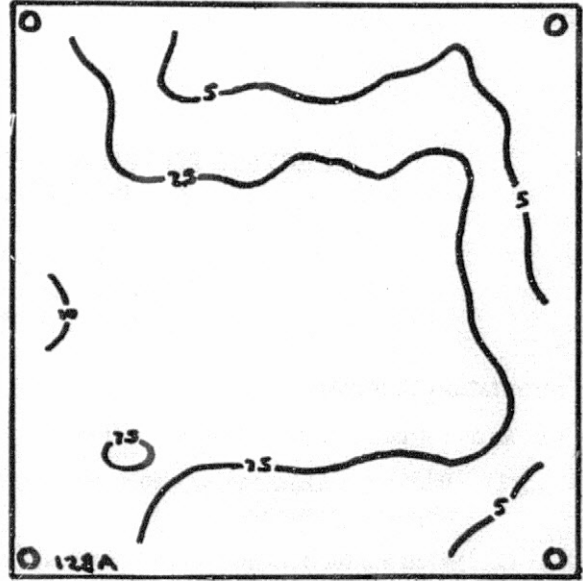


Fig. 7. New Cleaning Procedure: Alconox Scrub, Water Rinse, Acetone Rinse, Methanol Rinse, HNO<sub>3</sub> Etch

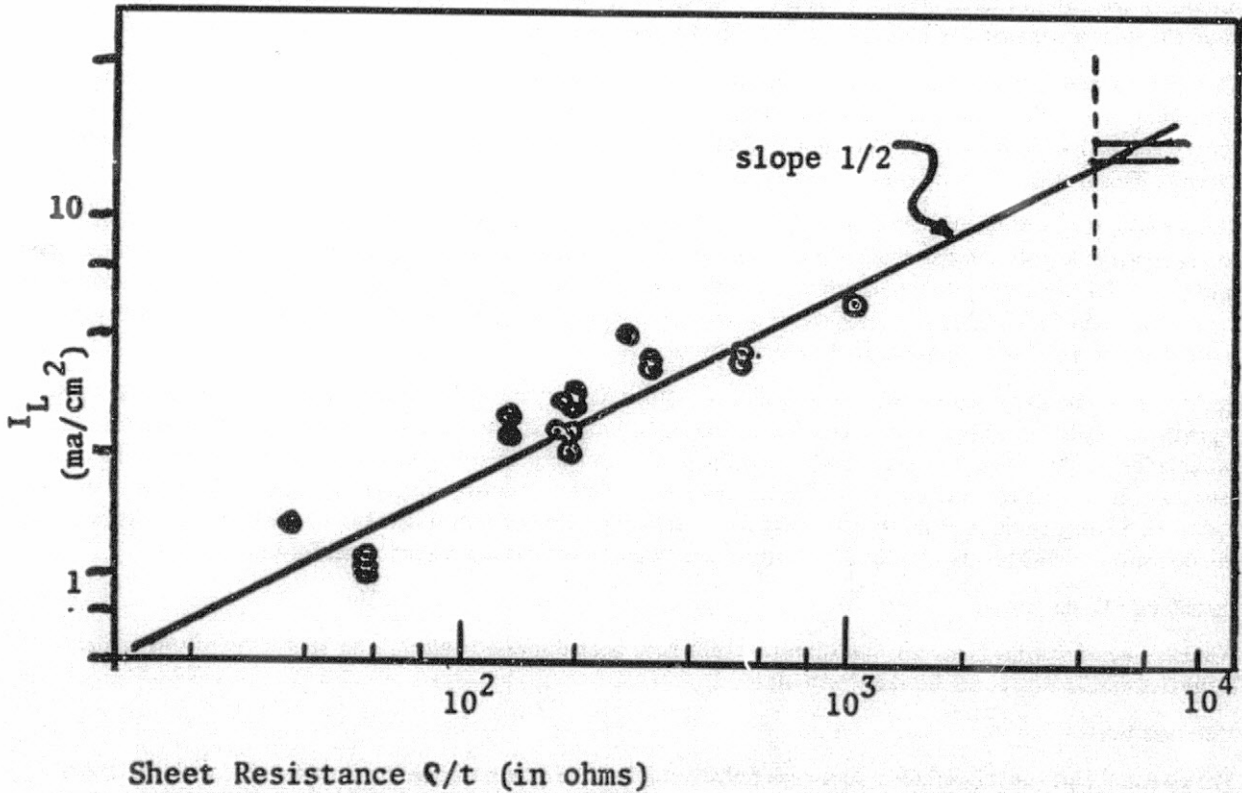


Fig. 8. Cu<sub>x</sub>S Sheet Resistance vs Light-Generated Current

## ELECTRIC POWER GENERATION THROUGH THIN FILM PHOTOVOLTAIC CELLS

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### Presentation Summary

From an industrial view, the following questions arise:

- (1) What types of generating plants could be built and how would solar power be introduced into the field of power generation?
- (2) What are the anticipated costs of installation per kW and of operation per kWh?
- (3) How long would the development take, how much would it cost, and how would it be funded?

Each of these questions will be considered in turn.

### Types of Plants

Solar cells are probably unique in the field of power generation in that they are indefinitely divisible into smaller subunits. The solar panel operating a roadside emergency call box has the same structure and differs only in area from the solar array that would be used in a 1000-MW generating plant.

Thus, a graduated penetration of solar power into practical applications is possible and probable, rather than an all or nothing approach. From gadgets to machinery to domestic power to industrial power – all the way to huge area generating plants feeding into a national grid – there is a ready-made gradation in size, power, and system complexity. This feature is important.

The lower-cost terrestrial thin film solar cells should find a ready market as components in portable and isolated location power supplies in the range of 1 to 1000 watts. Later it is possible they will be used in prefabricated solar roof panels for domestic power. An average suburban roof of 2000 ft<sup>2</sup> could supply about 18 kW during maximum insolation, and with suitable storage systems provide in the range of 50 to 100 kWh per day. This is significantly more than the usual consumption of the average house.

Scaling up to very-large-scale power generation is a major task in systems design and planning and will need many ingredients beyond the photovoltaic cell for its successful operation. As there are increasing indications that suitable low-cost photovoltaic cells can be developed, it is probably time to give serious consideration to the other aspects of large-scale systems employing them. An area of 100 X 100 km, representing only 0.1% of the total continental U. S. area, could provide several times the present total electric power demand of the U. S., and hence fulfill the demand forecast for the year 2000. A significant fraction of that is a realistic goal for solar cells.

### Installation Costs

Possible manufacturing costs for thin film solar cells have been discussed before. Our analysis confirms earlier estimates that the costs can be very low indeed.

### Materials Costs

The essential parts of the cell are: an n-type polycrystalline CdS film on a conductive substrate, with the upper surface of the CdS converted to p-type Cu<sub>2</sub>S; a semitransparent contacting electrode to collect and conduct the current from the Cu<sub>2</sub>S; and a transparent impermeable covering to protect the Cu<sub>2</sub>S.

A CdS film thickness of 5 microns maximum is a reasonable development goal and this can probably be achieved with a 50% utilization factor in deposition. Assuming CdS at a price of \$9.00 per pound and a 9% conversion efficiency, this represents a CdS raw material cost of 0.4 cents per watt of generating capacity.

A metal foil of less than 25 microns thickness could meet all the requirements for the conductive substrate. Electroformed copper foil has given good results and is available commercially at about \$2.50 per pound in thicknesses of 18 microns. Thinner material might be practical, and large quantity usage or lower-cost materials like aluminum might lower the cost appreciably. However, even this thickness of copper represents a substrate material cost of only 0.5 cents per watt.

Copper metal for an evaporated or otherwise applied grid and for positive leads would cost well below 0.1 cents per watt. All other miscellaneous raw materials used in the cell, including CuCl for forming the Cu<sub>2</sub>S layer and zinc or tin for forming an ohmic contact between the CdS and the copper substrate, would represent about another 0.1 cents per watt.

The only other raw material needed is some form of silica or alumina for a top covering for the cell. This coating has yet to be developed, but it is thought that 25 microns of pyrex glass would be adequate and could be applied in a variety of ways. Pyrex glass in powdered form would cost less than 0.5 cents per watt.

Thus, after suitable development and engineering, the total raw materials used in a mass produced CdS thin film solar cell should cost no more than 1.6 cents per watt of generating capacity. They might cost appreciably less.

#### Processing Cost

The CdS thin film solar cell is a flexible structure composed of metal foil, evaporated layers and chemically formed layers. Because of the simple geometry, high-speed processing of wide rolls of cells can be readily visualized. Linear processing speeds of several feet per second should be achievable eventually.

For estimating processing costs, the following assumptions are made:

Reel width: 3 ft  
 Production rate: 1 ft/sec  
 2 shift operation  
 Up time: 80%  
 Yield: 75%  
 Capital cost: \$2,000,000, written off over 5 years  
 Labor: 10 operators at \$20/hr including overhead  
 Cell efficiency: 9%

On these bases, production would average 6,000 square feet per hour, representing a generating capacity of 54 kW. The cost for capital would be \$100 per hour and labor and overhead would be \$200. Thus, the total processing cost would be \$300 per 54 kW, or well under 1 cent per watt.

Adding the material cost, the total solar cell cost is well under 3 cents per watt. This figure, however, is not directly comparable with the costs usually quoted for other forms of power generation, since the solar cell will only produce that power in full sunlight. While it is true that a lot of heavy electricity consumption coincides with the daylight hours, to get a good average 24-hour usage estimate and relate it to the availability of sunlight would require a separate study. For the present purposes we will arbitrarily assume that the "true" cost per watt of a general-purpose solar cell is of the order of 10 cents.

While these are order-of-magnitude calculations only, clearly more pessimistic assumptions could be made on both material and fabrication costs without affecting the final installation costs by very much. Also, more optimistic assumptions could be made for production rates and yields.

We have made ball park estimates of the cost of the other components of a complete solar power installation and have arrived at the following figures for round-the-clock operation:

Solar panels	10 cents/watt
Supporting structure	10 cents/watt
Construction and site preparation	5 cents/watt
Storage	20 cents/watt
Inversion	10 cents/watt

Thus, for a large area power station, a total installation cost on the order of 55 cents per watt, or \$550 per kW, is estimated. This compares with current coal-fired power station costs and favorably with nuclear station costs.

A 20-year life cycle for a solar power station, including the solar cells, panels, and supporting structure is a reasonable expectation. The costs of the inversion and storage components as described above were estimated on the same 20-year basis. Therefore, with 175,000 hours in 20 years, the capital cost for the entire generating system is \$550/175,000, or 3.2 mills per kWh.

For operating and final energy costs, it should be borne in mind that solar fuel costs nothing, presents no hazards, and does not pollute. With respect to maintenance and repair, one would confidently predict that a stationary array of cells, inverters, and storage systems will be significantly easier to maintain than the enormously complex present-day power stations, either of the turbine-generator or the nuclear type. However, even if the operation and repair costs represented half of the total power cost, which seems extreme, we get a total power cost of just 6.4 mills per kWh, which is a very encouraging figure.

#### Development

It is clear that rapidly increasing federal funding is going into all forms of energy research, including solar power. We believe that technical and (small-scale) economic feasibility of thin film solar cells could be established in about 3-5 years. The funding required would be very moderate indeed in view of the possible impact.

From the discussion above, it must be clear that the potential is enormous. All present trends in the energy field, now being treated at great length in just about every publication one picks up, favor a massive effort starting now. With such an effort, a timetable might be as follows:

Technical and economic feasibility (solar cells)	1976
Small-scale commercial applications (domestic)	1978
Medium-scale power (standby, industrial, remote areas)	1981-2
Large-scale solar power (contributing significant fraction of total capacity)	1985-90

#### Discussion

**Q:** I would like to ask what it is that Westinghouse is proposing to do? Would you just like to continue on with the processes as they are now known?

**A:** First of all we have to really get our feet wet in this area. We have done a lot of thin-film work, but we are new in these thin-film areas; so I think we would be much better to start now in the same direction as Professor Böer. I have suggested some new approaches which I don't want to discuss right now, but largely we are starting out in the direction that was shown by the Cleveite work and Professor Böer.

**Q:** Well, I am very happy to see that someone else picks up cadmium sulfide. I am also very happy to see that you have some optimistic figures. However, I thought I was reasonably optimistic, but now your optimism kind of scares me. You seem to have something which is one-tenth as expensive as what we had. I suggest that if we are very lucky and everything works out all right, we probably can go into the 15 to 20 cents a watt. But you have 2.6 cents a watt or so. Now that is one part. You seem to convert \$550 per kilowatt,

which I agree much more with, but you convert this into 3.2 mils, and that seems to be something which is possibly misleading. When I do the algebra, I take a five-hour day (average sunshine). I don't take your maintenance and so on, but just let me take the cost of money. So I take 10% cost of money, plus 2 or 2.5% of the linearized amortization over 20 years. I have taken 15 years. So it comes out as 12% per annum, and see what this can produce in terms of kilowatt hours per year. I come up with 2.5 cents and not 3.2 mils. And 2.5 cents is still all right when you put it on the consumer's rooftop, and you have it not as busbar but delivered price, so to speak, and adding a little bit of whatever is necessary for making power utilities happy, whatever their percentages are, so that they want to service the whole thing. So I come up again with a factor of 10, and I think for credibility reasons we should compare our numbers.

- A: This will be one of the purposes of the working groups. I would like to deal with it but I don't think we have time for it right now.
- Q: Is the drop in efficiency of cadmium sulfide with temperature about the same as that for silicon?
- A: It is about the same, but I do not have first-hand knowledge on this.

## SUMMARY OF THE NASA-LEWIS CdS SOLAR CELL PROGRAM

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### Presentation Summary

Between 1962 and 1971, the Lewis Research Center carried out a research and development program on CdS solar cells. The objective of this work was the development of a flexible, thin-film, large area solar cell that utilized materials and fabrication processes that ultimately could reduce the specific cost (\$/kW) and specific weight (kg/kW) of solar cell arrays for space power applications. The program consisted of an in-house R&D effort, contractual work with several commercial companies, and studies through university grants.

A pilot line was established at Clevite capable of producing large area (55 cm<sup>2</sup>) Kapton-covered Cu<sub>2</sub>S-CdS solar cells on a metallized plastic substrate. This line was required to produce 100 Class I cells per month. Class I requirements are shown in Table I. The line served as a source of cells for qualification tests and a base line from which changes in materials and fabrication procedures could be evaluated.

The average performance of Class I cells made on the pilot line for the last 3 years of the program is given in Table I. The percentage yield is the maximum yield obtained during one single month of the year. On several occasions no Class I cells were produced for the monthly period. Despite careful quality control procedures and considerable research effort, the causes of these slumps were never isolated. The problems would vanish as quietly as they came. As a result of this lack of control, steady, high yields were never achieved.

A large number of variations and modifications were explored as possible improvements in the cell performance and reproducibility. Some of these experiments are detailed in Table II. Every part of the cell from top to bottom was studied. Although some improvements were achieved, the major conclusion of the tests was that uncontrolled variables were significantly affecting the results.

Various life and storage tests were also performed. Some of these tests are detailed in Table III. In most tests, some cells would show remarkable stability while others would show large degradations. Analysis of the results suggested that the "vintage" of the cells was important and there were indications, unproven however, that the very substrate upon which the CdS was deposited sealed the fate of the cell. The one significant and reproducible degradation mode that was uncovered was the failure of the illuminated cell under open-circuit conditions. The failure was caused by electrochemical decomposition of the Cu<sub>2</sub>S layer into metallic copper where it contacted the substrate. Subsequent growth of copper filaments would short circuit the cell when they contacted the grid electrode. Unfortunately this failure mechanism was not the only one operating in the cell. Although cell voltage was controlled to prevent electrochemical decomposition, significant degradation of about 30% was still observed on vacuum-thermal cycling space chamber tests as well as on the other tests. It was finally discovered that a simple heat treatment in a hydrogen atmosphere could effect essentially complete recovery of all types of degraded cells except those damaged on high-temperature storage. It became clear that reversible stoichiometry changes were taking place in the Cu<sub>2</sub>S layer. It was also shown that the initial barrier layer as formed by the Clevite process was not stoichiometric Cu<sub>2</sub>S. The program ended before research efforts could be focused on these problems. Finally, total hermetic sealing of cells in epoxy resins and glass yielded cells that were stable in a room environment for years. Limited rooftop tests of these packages also indicated stability.

Although the Cu<sub>2</sub>S-CdS cell was produced for about \$70 per watt, unknown causes of yield, reproducibility and stability problems limited further development. These problems are complex and interrelated and must be solved before wide scale use of this cell can be effected.



**Discussion**

Q: Could you give us some concept of the magnitude of the program in dollars and also in number of cells?

A: The dollars that were spent were one to two million roughly. I think that's about the proper magnitude. It reached a peak of around 200 to 225 thousand a year.

Q: Was that external or internal?

A: That's external. These are all contract dollars. The number of cells that were produced seemed legion and countless. I know right now we've got several thousand cells.

C: I can answer that point. It was somewhere between 100 and 200 thousand 3-inch by 3-inch cells.

C: I think the point of my question is that that is still not a significant amount of cells or money to be spent before saying that this problem is viable.

C: I think it should be pointed out that the French have a fairly extended effort going on, and they are going to be reporting on it at the Photovoltaic Conference. And the Germans, also. The French claim they have solved a lot of these problems.

C: I think two things may be pointed out here. One, of course, that your restraints, your measurements, and saying whether the cells are useful or not are especially space-oriented. For instance, temperature cycling. That is a very major factor because of the differential thermal expansion, separation of grids, and so on, which is a much more severe problem for space than it is for ground. And so some of the selections which have been done there need to be rechecked.

C: The other point is if we could make one cell which has a good property for a long enough lifetime, we know that it is not against the second law of thermodynamics. And then the other thing is what we call production yield. The production yield may be poor – we think it is poor – but now this affects the figure of what it finally will cost to make these cells, because you have to have testing in order to select what is a good cell to start with. Then, of course, you can use only part of it. However, this is amenable to research, and I want to point out here to NSF and other sponsoring groups that with one or two million dollars you can go on forever and ever and ever. Now it would take a tremendous amount of time and you would forget at the end what you did at the beginning. You have to have a concerted research effort to solve these problems and they are major problems. Then what is the un-reproducibility? Take just this dipping method which is such an unreproducible kind of thing, in which you have Reynolds numbers and what have you. There is a tremendous amount of material which has to be diffusing within five or four seconds. So I think a concerted research effort is necessary if we want to make good cadmium sulfide cells. I am convinced that it can be done, but I think that needs to be said.

C: There are a few points I'd like to make. One is that we have shown that in single-crystal cadmium sulfide, there are definite changes that have taken place. There are, under ion implantation, where you destroy some of the crystallinity of the material, temperature annealing processes which go on, and these have been shown by other workers in England to go on even in temperatures as low as liquid nitrogen. So even at room temperature you can expect changes to occur if the material is in a metastable state, as would be the case when you have a junction between CdS and copper sulphide. Secondly, the material at room temperature will absorb or adsorb large amounts of nitrogen, so that dry nitrogen gas itself will not resolve the problem of not getting trapping centers associated with nitrogen on the surface. These are easy to remove under mild heat treatments in vacuum on single crystals, but I have no idea what this would do on polycrystalline layers. So just keeping them in a dry nitrogen atmosphere is not going to solve the problem.

Q: To summarize, I want to obtain your expert opinion. Would you like to see NASA get back into CdS?

A: Now, that's a tough question! You have to keep in mind that NASA is directed at space, and our current goal is to reduce the cost and to raise the efficiencies of space arrays. Ultimately, if we raise the efficiency, it will reduce the cost. I don't know whether CdS fits in with that goal.

Table I. Summary of Production of Kapton-Covered Cu<sub>2</sub>S-CdS Cells on Clevite Pilot Line

Class I Cell Requirements			
	Eff. $\geq$ 2.8%		
	F. F. $\geq$ 68.5%		
	SCC <sub>60°C</sub> $\geq$ 0.98 SCC <sub>25°C</sub>		
Average Cell Performance, AMO, 25°C			
	1969	1970	1971
SCC, amp	0.761	0.785	0.798
OCV, volt	0.469	0.464	0.472
P <sub>MAX</sub> , watt	0.250	0.254	0.260
F.F., %	70.1	69.5	69.3
EFF., %	3.3	3.3	3.4
MAX. YIELD, %	41.	32.	46.

Table II. Partial Listing of Experimental Program

Experiment	Variables	Best Result
Substrate material	Glass, Cu, Mo, Kapton	Kapton
Coating material	Cu, Ag, Zn, Ag-Pyre ML	Ag-Pyre ML
Coating technique	Sprayed, roll coating	Roll coating
Interlayer material	Cr, Cu, Zn	Zn
CdS deposition	Sprayed, sputtered, evap.	Evaporated
Barrier formation	Slurry paint, electroplate, chemiplate	Chemiplate
Heat treatment study	High temp/short time } Air Low temp/long time } Vac	Varied
Grid material	Cu, Ag, Au, Au/Cu	Au/Cu
Grid attachment	Pressure, evap., elec. plate, Au-Epoxy	Au-Epoxy
Cover plastic	Tedlar, Mylar, FEP, Kapton	Kapton

Table III. Cell Life Tests

Test	Time Period	Degradation
Dry shelf, room temp.	4.5 yr	0-10%
Humidity, 80% RH, room temp.	2.0 yr	20-25%
Const. illum., open circuit	Few days	~50%
Outdoor ambient	3-6 mo	Varied according to plastic encapsulant Kapton best
Thermal vacuum, 100°C, 10 <sup>-4</sup> torr	0.5-1.0 yr	0-50%
Simulated orbit test	1.4 yr (8,000-10,000 orbits)	5-30%

## DEFECT STUDIES IN SOLAR CELL MATERIALS

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## Presentation Summary

## Introduction and Background

The correlation of defect type, structure and density with normal electrical properties (conductivity, mobility) has been reported for a number of materials (Refs. 1-4). The relationship between the presence of a particular defect and its influence on the electronic character of the material is usually explained in terms of some scattering mechanism. The effect of these defects depends primarily on their density and nature. Those of importance to this paper can be classified as follows: (i) point defects (vacancies), (ii) line defects (dislocations), (iii) plane defects (surfaces, grain boundaries, stacking faults, twin boundaries, phase boundaries), and (iv) volume defects (voids).

The investigation of the effects of scattering from grain boundaries (Ref. 1), surfaces (Ref. 1) and stacking faults (Ref. 2) in CdS thin films has demonstrated the significance of these planar defects in determining film resistivity and mobility. Incorporating grain boundary (Petritz) scattering and surface scattering theories with the effects of diffuse scattering from stacking faults, leads to the general relationship for film mobility (Ref. 2):

$$\mu = \mu_0 \left\{ 1 + m^* \exp \left[ (q\phi_{sf} - q\phi)/kT \right] \right\}^{-1} \quad (1)$$

where

$$\mu_0 = \mu_b \exp(-q\phi/kT)/(1 + \lambda/d) \quad (2)$$

In these expressions,  $m^*$  is the effective number of stacking faults/grain;  $q\phi_{sf}$  and  $q\phi$ , the stacking fault and grain boundary scattering potentials respectively;  $\mu_b$ , the bulk material mobility;  $d$ , film half-thickness; and  $\lambda$ , the mean surface scattering length. Therefore, Eq. (2) represents a special case of Eq. (1) – that with no faults present.

The relative effect of each of these defect types is closely related to the growth conditions or deposition parameters for the films. Figure 1 shows the relationship between film mobility and grain size (and resulting grain density) which is a function of substrate temperature. The data of Fig. 2 illustrate the dependence of film resistivity on stacking fault density which in turn depends on substrate temperature. Finally, Fig. 3 indicates the surface scattering length,  $\lambda$ , dependence on this parameter (Ref. 4).

## Present and Proposed Research

The research effort relating to defect studies in solar cell materials is being undertaken in three categories: (1) The continuation of the defect investigations mentioned for CdS as well as the expansion of this work to other defects and other materials including Si, Cu<sub>x</sub>S, CdTe, CdSe, PbTe, and InSb – in single-crystal, polycrystalline, and amorphous forms, and (2) The investigation of the photoconductive contributions of defects to these materials. Some work in this area has also been reported, including photocurrent and photoconductivity enhancement due to stacking faults (Ref. 5). The examination and determination of defect related photo properties is of special interest to this study; and finally, (3) The determination of optimum fabrication parameters, based upon the defect studies, to maximize the electrical and photo properties by minimizing or maximizing the particular effects of point, linear, and planar defects. This includes the complete investigation of current and projected fabrication techniques – especially the evaluation of effects of junction production on the creation of these defects.

This entire investigation is in its initial stages. Work relating to categories (1) and (2) has begun for defects in polycrystalline Si and Cu<sub>x</sub>S and void properties in amorphous Si. It is expected that the work in category (3) will be started in approximately 3-4 months for Si and CdS cells. Cooperation will be sought and needed from laboratories producing such cells or initiating new techniques which might need evaluation.

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### Discussion

Q: Are you proposing to make cells and at the same time ---?

A: We are going to be studying the effect of production techniques on forming the CdS/Cu<sub>2</sub>S junction on the presence of stacking faults in the junction region. Many times metallurgically adding copper to the system increases the stacking fault energy of the system, and we get some evidence of this in the cell itself.

Q: Of course, you are quite aware that your results are very much dependent on what kind of substrate you are using.

A: Yes.

C: And so glass is completely different from metal or conductive substrates which you need to use for cadmium sulphide evaporation. I think that I should point out something which often is misunderstood. I think that 8.3 is the highest percent of cell efficiency that is documented. I think I should discourage people from thinking that cadmium sulphide could be made way and above ten percent. It is a heterojunction which we have and not a homojunction. Hence, we have essentially single-carrier conduction, and the limits of efficiency seem to be in the neighborhood of close to ten percent, a little above or below. And of course, given this, it would make very little sense for NASA to go into CdS to compete with averages above ten percent, since it is the deployment cost in outer space that is more important than the cell efficiency.

Q: You mentioned the photoconductivity studies. Have you in any way related your photoconductivity studies to the photovoltaic studies, or are these an entirely separate area?

A: No, I am taking that whole area, hopefully.

Q: You mean both photovoltaics and photoconductivity?

A: Right.

Q: You are trying to establish relationships between them?

A: Correct. The relationship is established through the spread of the quasi-Fermi level, and this is very important for the photovoltaic effect. Although what happens in the cadmium sulfide doesn't seem at first view to be related to the photoconductor properties, in a way it is because of the photoconductivity levels.

Q: How do you separate the effects of stacking faults from the effect of grain boundaries in the polycrystalline material?

- A: It is due to the anisotropy. Cadmium sulfide, if you are very careful, grows with the C-axis perpendicular to the substrate. This is by vacuum evaporation. The grain boundaries in our model are perpendicular to the substrate, so that if you take measurements along that direction, you get the grain boundary contribution and the surface contribution. But if you take the cross-plane measurements, the major faults in the CdS are C-plane faults, so that they lie parallel to the substrate. So you can get both of these effects due to the anisotropy. But we have done some work where we have made films which have the stacking faults, where we have the grains at angles to the substrate and got both effects in there. We showed effects of both grain boundary surfaces and faults combined.

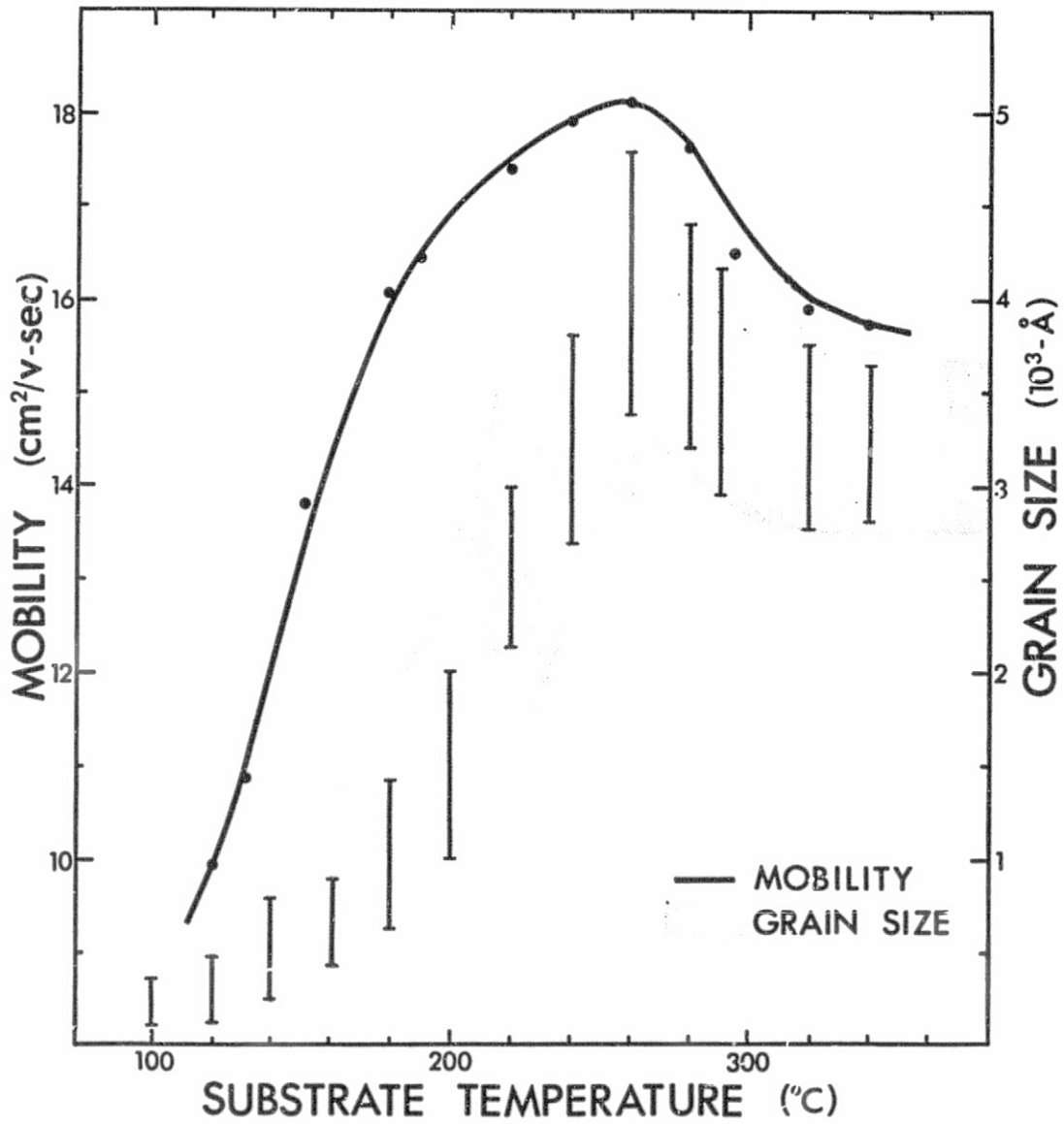


Fig. 1. CdS film mobility and grain size as a function of substrate temperature indicating dependence of mobility on grain size and resulting grain boundary density

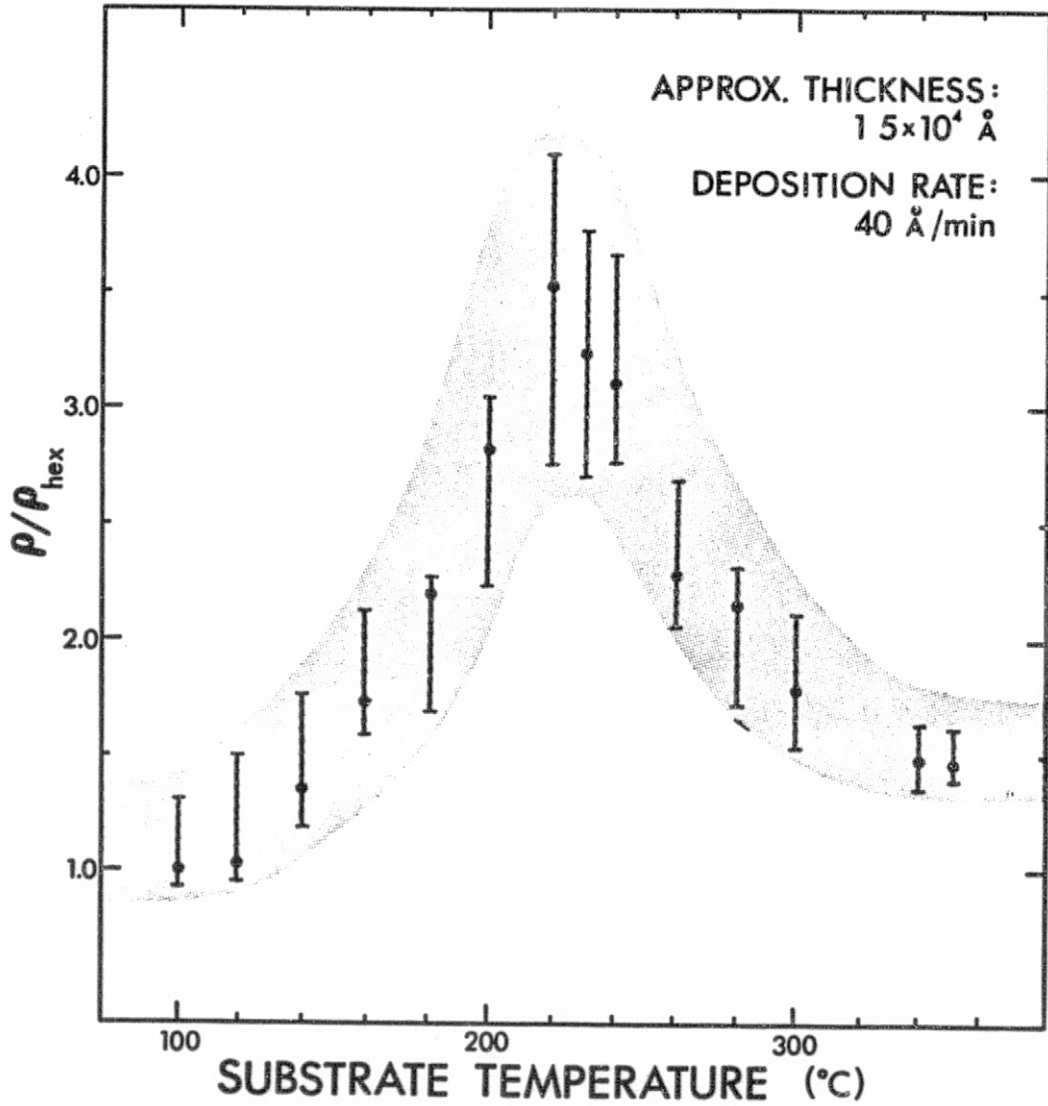


Fig. 2. Dependence of film resistivity,  $\rho$ , on substrate temperature for films indicating maximum resistivity at point of greatest stacking fault density;  $\rho_{\text{hex}}$  is the resistivity of unfaulted films



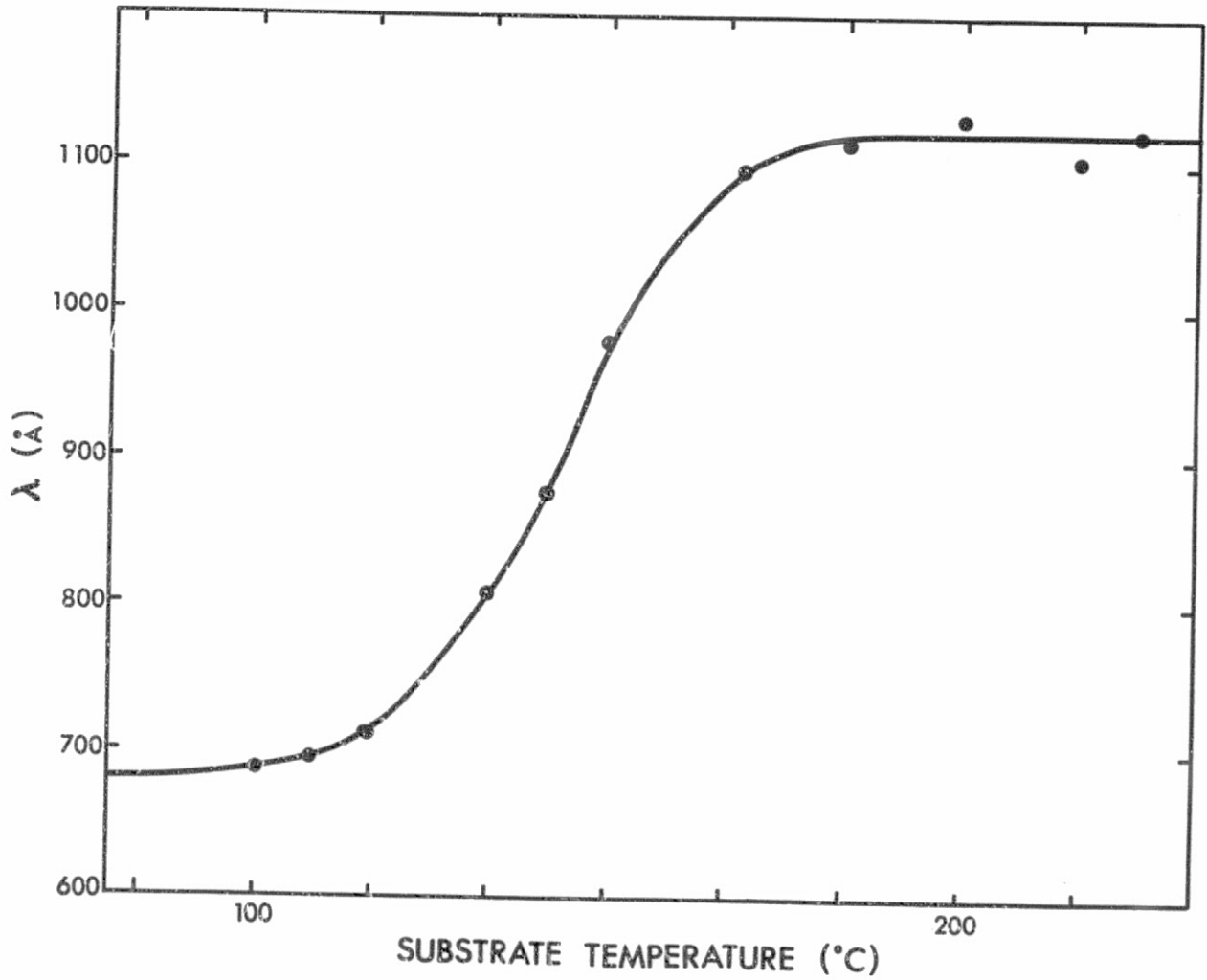


Fig. 3. Mean surface scattering length,  $\lambda$ , as a function of substrate temperature for CdS thin films. Data indicate that  $\lambda$  increases with decreasing carrier concentration

## DEVELOPMENT OF LOW COST SOLAR CELLS

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### Presentation Summary

The direct conversion of sunlight to electricity on a large scale is economically dependent upon the ability to produce a low-cost solar cell. Laboratory experience at the D. H. Baldwin Company indicates that it is economically and technically feasible to make thin film photocells of approximately 5% efficiency at a cost of less than \$60.00 per peak kilowatt (6¢ per peak watt).

This is made possible by adopting the techniques of the glass making industry, in particular, the float glass process. In this process, the materials for the manufacture of glass are melted in a continuous type furnace. Raw materials are continuously loaded in one end of the furnace and the molten glass poured out of the other end onto a molten bath of tin. The rate at which the glass is moved over the tin bath and the supply of molten material determine its thickness.

Thin films of CdS (approximately 2 microns thick) are grown by spraying suitable chemicals on the moving ribbon of glass while it floats on the surface of a molten tin bath. Prior to spraying the CdS, a solution containing a tin compound is sprayed on the glass to produce an SnOx film which acts as the negative electrode of the cell.

Other chemical sprays are directed onto the surface of the cadmium sulfide film, at a lower temperature, to produce a Cu<sub>2</sub>S heterojunction. The final step involves cutting the glass into sheets of suitable size, and vacuum evaporating the necessary electrode patterns.

### Solar Cells

Among the various types of solar cells are two upon which extensive research and development work has been done. These are silicon and cadmium sulfide:

#### Silicon

While silicon is an excellent material for such cells, its cost of processing is such that even in large-scale use, its cost per kilowatt will be \$6,000.00 (Ref. 1). This is still a long way from the approximate \$200.00/kW cost of a conventional coal-fired power plant.

#### Cadmium Sulfide

Another material which has had considerable study over the past several years is CdS (Refs. 2-5). The cells were generally made by vacuum evaporation of CdS onto flexible metallized substrates. The resulting CdS film bearing substrate was then immersed in a CuCl solution to provide a Cu<sub>2</sub>S heterojunction, after which a conductive grid was brought into contact with the film to form a positive current collecting electrode (Refs. 6-9).

On cells of this type, which were intended for use in space and were therefore of light construction on a plastic film base, a number of difficulties were encountered. There were mechanical problems due to the thermal cycling under simulated space conditions, later corrected, and a gradual deterioration under load. The barrier was also sensitive to degradation by water vapor.

Since the CdS cells which are the subject of this proposal are radically different in construction, the most serious concern is that of degradation under load. This is apparently due to a breakdown of the Cu<sub>2</sub>S into CuS and Cu which occurs at 0.38 volts (Ref. 9). By operating the solar cells at the output voltage producing maximum output (0.31 to 0.33 volts) this degradation effect is minimized.

#### Description of the Cell

The construction of the solar cell proposed is shown in Fig. 1. It uses float glass (1/8 - in. double strength window glass) as a substrate. It is a back-walled cell; that is, the solar radiation passes through the glass.

Upon the glass surface (glass is a microscopically smooth and inexpensive substrate) is grown, by spraying, a thin film of SnOx, a conducting transparent conductor, which serves as the negative electrode. Upon the SnOx film, a layer of polycrystalline CdS is grown (approximately 2 microns thick) and over this a layer of Cu<sub>2</sub>S which, after proper heat treatment, serves as a heterojunction.

Contact is made to the negative SnOx electrode at frequent intervals by means of a grid structure. This structure is composed of a thin layer of Inconel covered by a thicker layer of copper or aluminum, both evaporated through suitable masking. The positive electrode consists of a layer of copper, also evaporated through a mask, which covers the entire active area of the cell. This copper layer helps to protect the barrier from water vapor and other contaminants.

#### Requirements for Solar Cell Producing Large Amounts of Power

Solar cells, to be economically feasible, should satisfy the following requirements:

- (1) Low cost (a thermal generating plant presently costs approximately \$200.00/kW).
- (2) Should not place a great demand on scarce materials.
- (3) Have reasonable life.

#### Cost

To obtain the cells at approximately 6 cents/watt, it will be necessary to manufacture on a very large scale. We propose to use existing technologies throughout. As a case in point, the process starts with a float glass plant (see Fig. 2), which is presently the preferred method of making glass. In such a plant, glass is manufactured in a continuous ribbon. The raw materials are continuously fed to a furnace and melted. The resulting liquid is poured onto a bath of molten tin where, by controlling the feed rate of materials and velocity of the glass ribbon, its thickness can be controlled within  $\pm 0.002$  in. The glass used is 1/8 in. thick (so called double-strength window glass). Glass is fed as a continuous ribbon 10 ft wide from the liquid tin bath to a cooling lehr, where it is cooled before being automatically cut to size. A typical annual output for such a plant would be 200 million square feet per year. A recently completed plant of this type, using two production lines such as described above, has a planned capacity of 400 million square feet of glass annually. The plant cost 50 million dollars.

We propose to interpose, between the present liquid tin bath and cooling lehr, three more liquid metal tanks (see Fig. 3). The first of these will be used for spraying a tin compound and dopants to provide a conducting SnOx layer. The second will be used to spray the CdS film, and the third, in the cooling line at a much lower temperature, for spraying on the Cu<sub>2</sub>S layer. After some further cooling, the glass will be cut automatically to size. After cutting, it will be fed to an automatic vacuum evaporating line with suitable masks for evaporation of the electrodes. A short reheating cycle in air is then necessary to optimize results.

There is a process, upon which we have done some work, which does not require screening and etching. In this process, evaporated zinc is used as the negative electrode. Upon heating, the zinc diffuses through the barrier (through the Cu<sub>2</sub>S into the CdS) and contacts the CdS layer underneath. The current then passes through the CdS layer twice (see Fig. 4)

It should be emphasized that in our laboratory the various steps of the above-described processes have been tested by batch methods.

SESSION IV. CdS/Cu<sub>2</sub>S THIN FILM CELLS - JORDAN

Cost: Exclusive of Installation, Site Preparation, and Power Handling Equipment

Materials	Cost, dollars/ft <sup>2</sup>
Glass, <sup>a</sup> 14¢/ft <sup>2</sup>	0.1400
Other materials (chemicals and metals)	0.0509
Total materials	0.1909
Depreciation charges	0.0150
Maintenance	0.0100
Power	0.0050
Additional labor costs incident to cell manufacture	0.0018
Additional G and A	0.0165
Total cost per square foot	\$ 0.2392

At 5% efficiency, one square foot of glass will produce a peak power of 4.645 watts.

Cost per peak watt	\$ 0.0515
Cost per peak kilowatt	\$ 51.5 <sup>(1)</sup>

<sup>a</sup>Actual glass costs are closely guarded by the glass industry. We have good reason to believe that it is less than 14¢/ft<sup>2</sup>.

#### Scarce Materials

The only material which is not produced in great quantity is cadmium. It is for this reason that films of approximately 2 microns thickness were chosen. This thickness would entail the usage of 45,000 lb of cadmium per square mile. A square mile of cells would produce 129,000 peak kilowatts. The present annual usage of cadmium in the United States is approximately 10,000,000 lb (Ref. 10). The demand and price are very variable, depending on economic conditions. It is believed that the supply could be greatly increased if a steady demand existed.

#### Life

No meaningful life data is available for the cells in question. However, there is no reason to believe that their life would be less than those of previous CdS-Cu<sub>2</sub>S cells, although there is a possibility that they will be better in this regard. The junction is not made by immersing the CdS film in a CuCl solution, which is highly active chemically. Instead, it is made by spraying a solution of copper acetate and N,N, dimethylthiourea in deionized water onto the CdS. Chlorine, which is extremely active chemically, is not present as it is in the other process.

More recent tests for cadmium sulfide cells by others (Ref. 9) have shown that operation of the cell below 0.38 V, as mentioned previously, indicates that cell life is greatly improved.

Ionic mobility has been reported by others (Ref. 11) when making I-V plots on evaporated cells at a very slow rate. We have not been able to detect such an effect while making I-V plots on the sprayed type cell.

There is another factor affecting cell life as pointed out by Haynos (Ref. 12). This is the effect of infrared radiation. Tests of evaporated cells under xenon solar simulators show considerably less degradation than when tested under tungsten halide sources, rich in infrared. Haynos points out that it is the infrared component which accounts for the degradation.

In the case of the sprayed cell (which is a back surface cell) the glass substrate-SnOx layer combination discriminates against infrared (see Fig. 5). The transmission of wavelengths longer than 0.7 microns falls off rapidly.

#### Present Status of the Development

Cadmium sulfide cells have been made by a number of investigators with efficiencies extending to 8% (Ref. 13). Most of the cells reported upon in the literature have been made by the vacuum deposition process.

CdS solar cells of 3.5% efficiency, made by spraying chemicals on heated glass, were reported by Chamberlin (Ref. 14) and Skarman 10 years ago. The yield of good cells, however, was very low.

For the past three years, the D. H. Baldwin Company has been studying the growth of CdS crystals on glass by spraying chemical constituents upon the glass surface while it is heated. During the spraying process the glass rests on the surface of a molten tin bath maintained at temperatures between 350 and 430°C. This process is of interest because it permits low cost production as described above.

By adding an additional step, successful growth of crystal films, consisting of grains from 2 to 12 microns in the dimension parallel to the substrate, has been attained (see Fig. 6). In the vacuum deposition process the crystallites are generally 0.1 micron or less on the same dimension. A further characteristic of these films is their high specific resistivity, as grown, which varies between  $10^3$  and  $10^5$  ohm-cm. This is due to the fact that the crystals grown at the temperatures noted above tend to be stoichiometric and reject impurities. Crystallites grown by vacuum deposition generally have specific resistivities between 0.1 and 1 ohm-cm due to an excess of cadmium inherent in the vacuum evaporation process.

Cu<sub>2</sub>S layers have been grown on the CdS films by spraying a solution of copper acetate and N,N, dimethylthiourea while the glass substrate rests on a liquid metal bath, maintained at a temperature of approximately 150°C.

The above processes have been done in air although it is probably advisable, at least in the growth of CdS, to use an atmosphere consisting of a mixture of N<sub>2</sub> and H<sub>2</sub> to prevent oxidation of the tin, which is expensive.

Sufficient cells have been made using commercially available SnOx coated glass of 50 ohm/square and undoped CdS to indicate that large-area cells of 5% efficiency are feasible. In probing a cell area of 105 cm<sup>2</sup> with 16 1 cm<sup>2</sup> probes, 15 of the test points have indicated voltage of greater than 400 MV, a criterion we have found to be indicative.

In order to make cells of 5% efficiency one must use SnOx coated glass with a resistivity of 10-15 ohms/square. Since this is not commercially available, our primary effort during the past several months has been devoted to this problem.

We have now succeeded in depositing SnOx films of 10 ohms/square on soda line glass with a resulting transmission (including the glass) of 78%. The SnOx film itself transmits 92% of the incident radiation. This has been a difficult problem because the crystal structure of the SnOx controls the ensuing growth of the CdS film, which in turn controls the growth of the Cu<sub>2</sub>S film. It is necessary that the growth of each of these films be uniform to produce useful cells.

By coating the barrier with copper, the cell resistance can be greatly lowered as the sheet resistance of the Cu<sub>2</sub>S is then no longer important. In addition, the metallic copper coating serves to help protect the barrier from atmospheric contamination. An additional coating of aluminum over the copper gives further protection. Both coatings can be evaporated in less than a minute in a continuous vacuum evaporation setup.

#### Problem Areas

1. Since the specific resistivity of the CdS, as grown, is very high, as mentioned previously, it is necessary to dope the film to produce a lower value. We are presently adding aluminum to the spray solution and have reduced specific resistivity by two orders of magnitude. This entire area needs further investigation and evaluation.

2. Further optimization of the CdS and Cu<sub>2</sub>S film thicknesses should also be investigated.
3. Method of protecting the barrier (metal films are helpful).
4. Life test of completed cell (we have no life test setup at this time but we intend to construct equipment for outdoor testing in actual sunlight in the near future).

#### Conclusion

It appears feasible to produce thin film CdS-Cu<sub>2</sub>S solar cells at a cost which would permit the large-scale utilization of solar power by photovoltaic means in the not too distant future. The problems of power handling and energy storage, however, will have to be dealt with before such utilization can be realized.

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**Discussion**

Q: Have you obtained some cells?

A: Yes.

Q: I see. In the original paper it was claimed that the cells have output voltages in the neighborhood of 0.9 volts or so. Another reason why cadmium sulfide is not so efficient is that the interface between cadmium sulfide and copper sulfide is about 0.85 electron volts and you need to have a barrier to prevent back tunnelling; this essentially reduces the output voltage to below 0.6 or 0.55 volts. That is one of the major reasons why cadmium sulfide isn't so good compared to silicon. Now this 0.9 volts – this is kind of scary – the theory doesn't seem to fit. Do you have any information?

A: That is quite correct. I got out some of the early cells made about seven or eight years ago and they still have rather high voltages, but the currents obtainable from those were very low. And actually, our open-circuit voltage is now about 420 millivolts and it agrees with your information. What we have done is really what you find. The critical question we must ask ourselves in this particular process is: Is cadmium sulfide a suitable material for power under load? Does it have suitable life under load? I cannot answer those questions. I have to defer to some of the other worthies here. This is merely a method of doing it inexpensively should it become viable to do so. Of course the power handling and the immense power storage problems would have to be solved. But this can be done with existing technologies. No technical breakthroughs are necessary, and these processes have all been tried in our laboratory.

Q: I am so intrigued with your flow diagram here that I didn't quite get to the end. What did you finally encapsulate this with?

A: The glass faces the sun so that it is protected in this regard, and the active areas are covered with copper, which is evaporated. We have found a method of evaporating copper so that it doesn't short-circuit the cell. We do it by introducing oxygen into the spray. The cell does not become activated until you heat the whole thing, at which time there is a reaction that goes on between the copper, the copper sulfide, and the oxygen.

Q: One question is in terms of the power need. Can you compare the power for evaporating CdS to that required for a large amount of water?

A: It is quite reasonable, actually. The most expensive part of our system is the vacuum evaporation. That cost is 35 million dollars as a total. The total plant cost would be over 100 million. What the power industry uses is five billion a year to increase its facilities; so that's not bad.

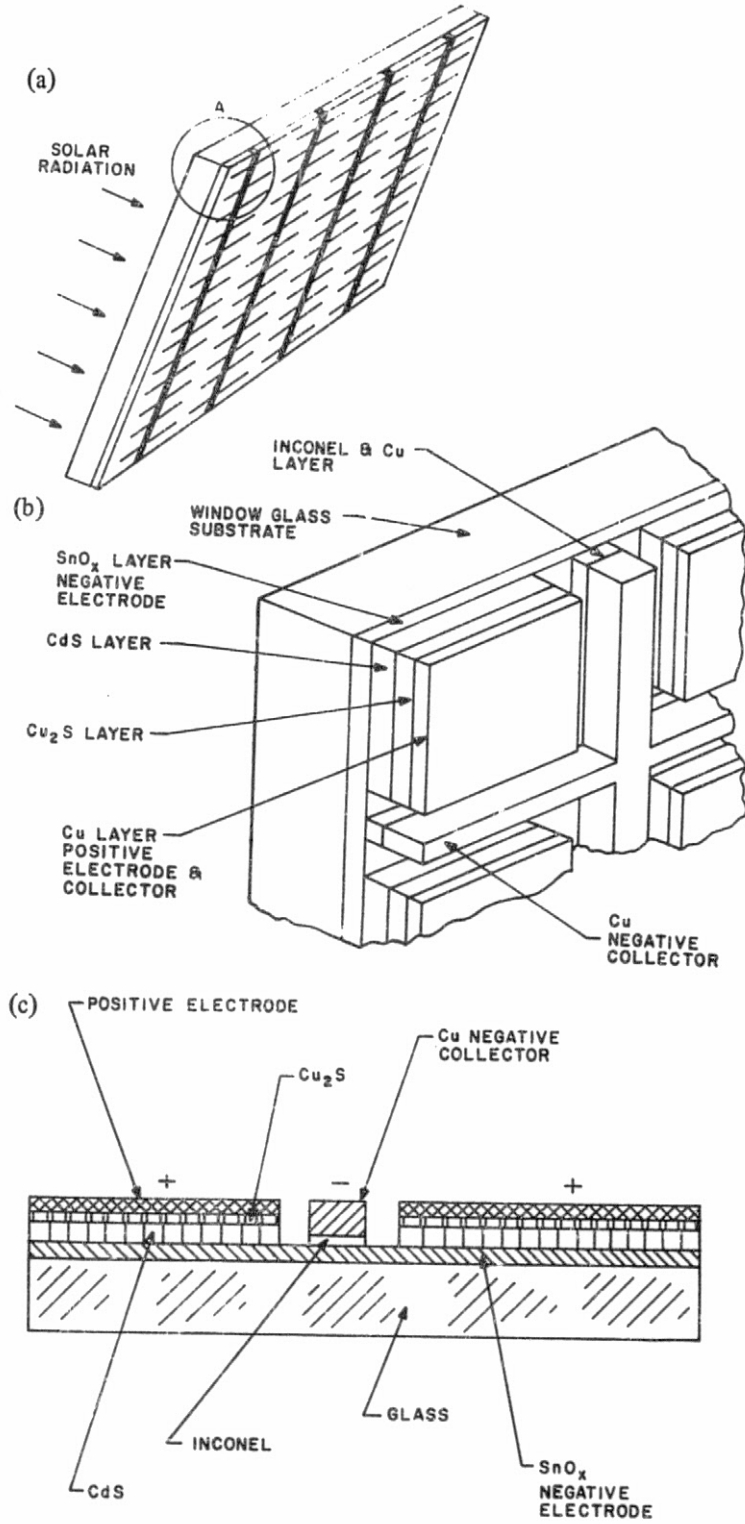


Fig. 1. Solar Film Cell: (a) Cell, (b) Enlarged Detail of Cell, (c) Cross Section of Cell



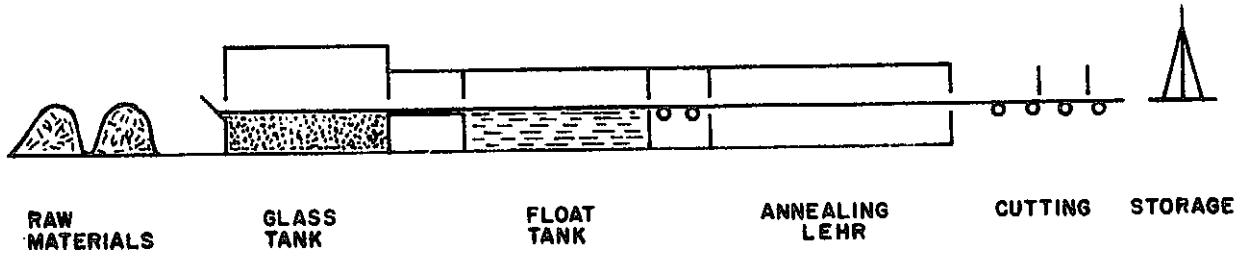


Fig. 2. Schematic of Typical Float-Glass Plant

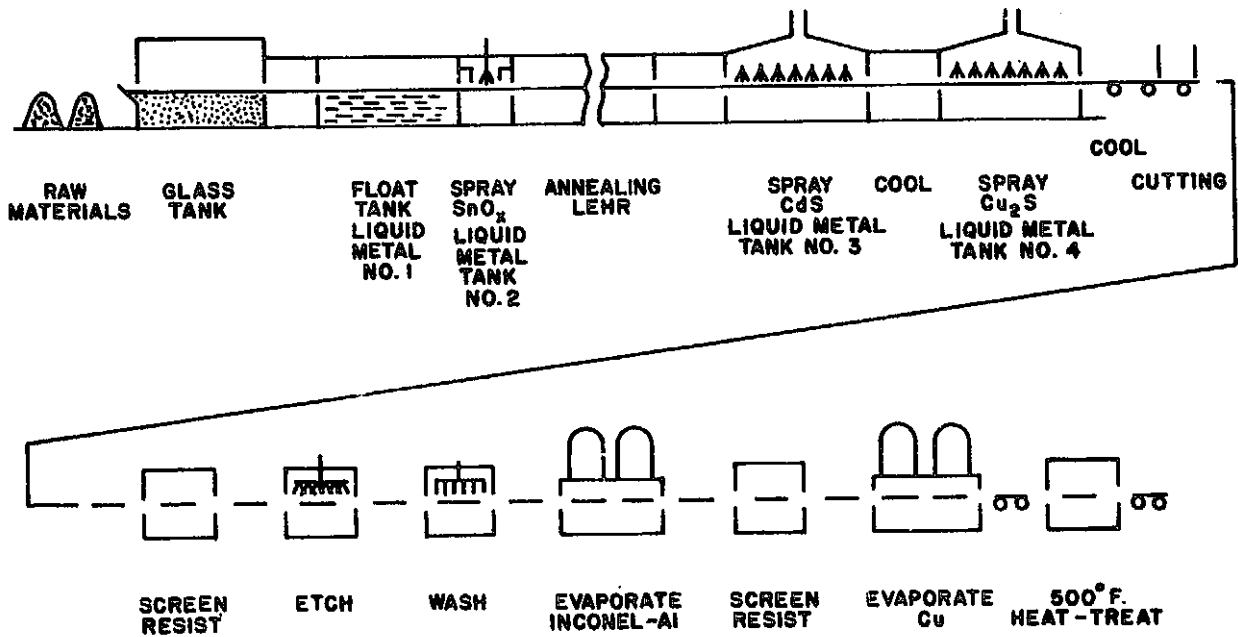


Fig. 3. Schematic of a Float-Glass Solar-Cell Plant

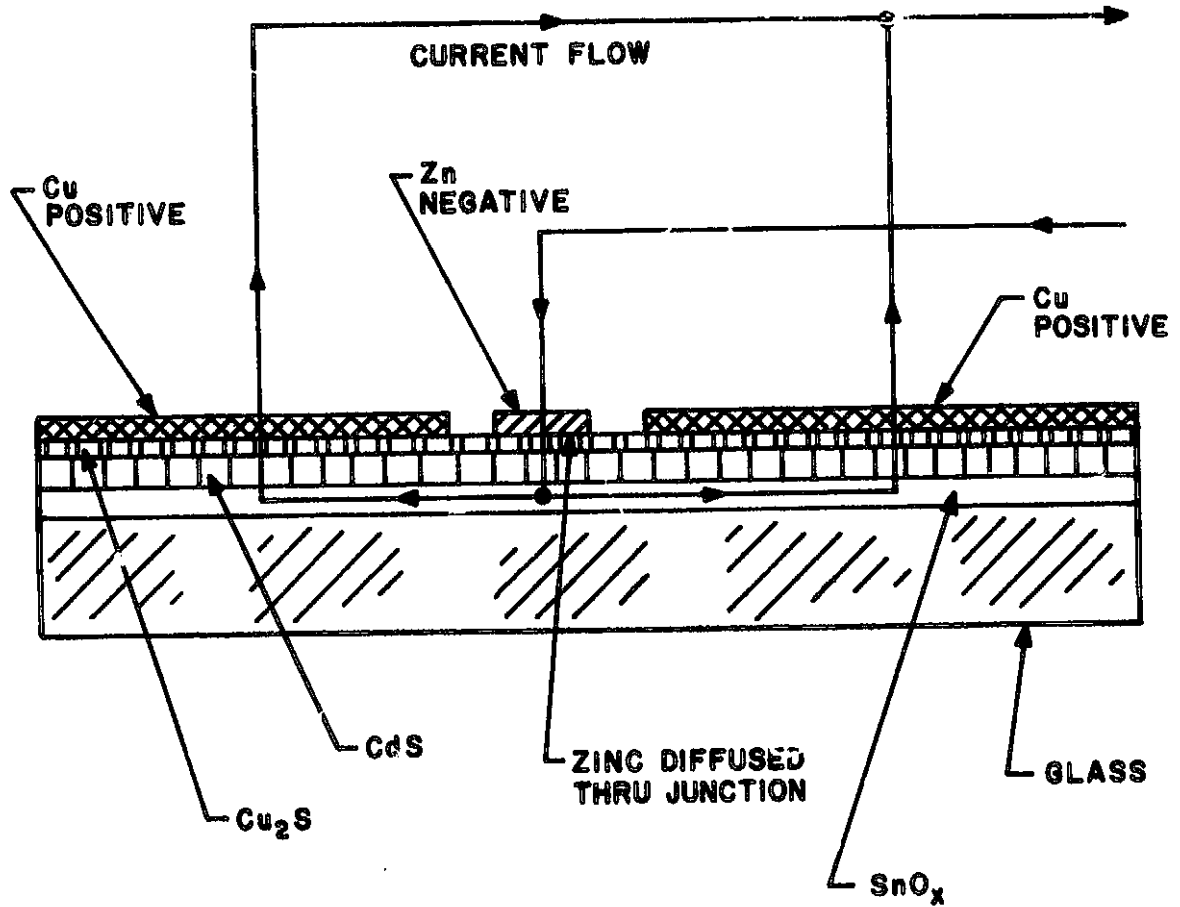


Fig. 4. Diffused Zinc as Negative Collector

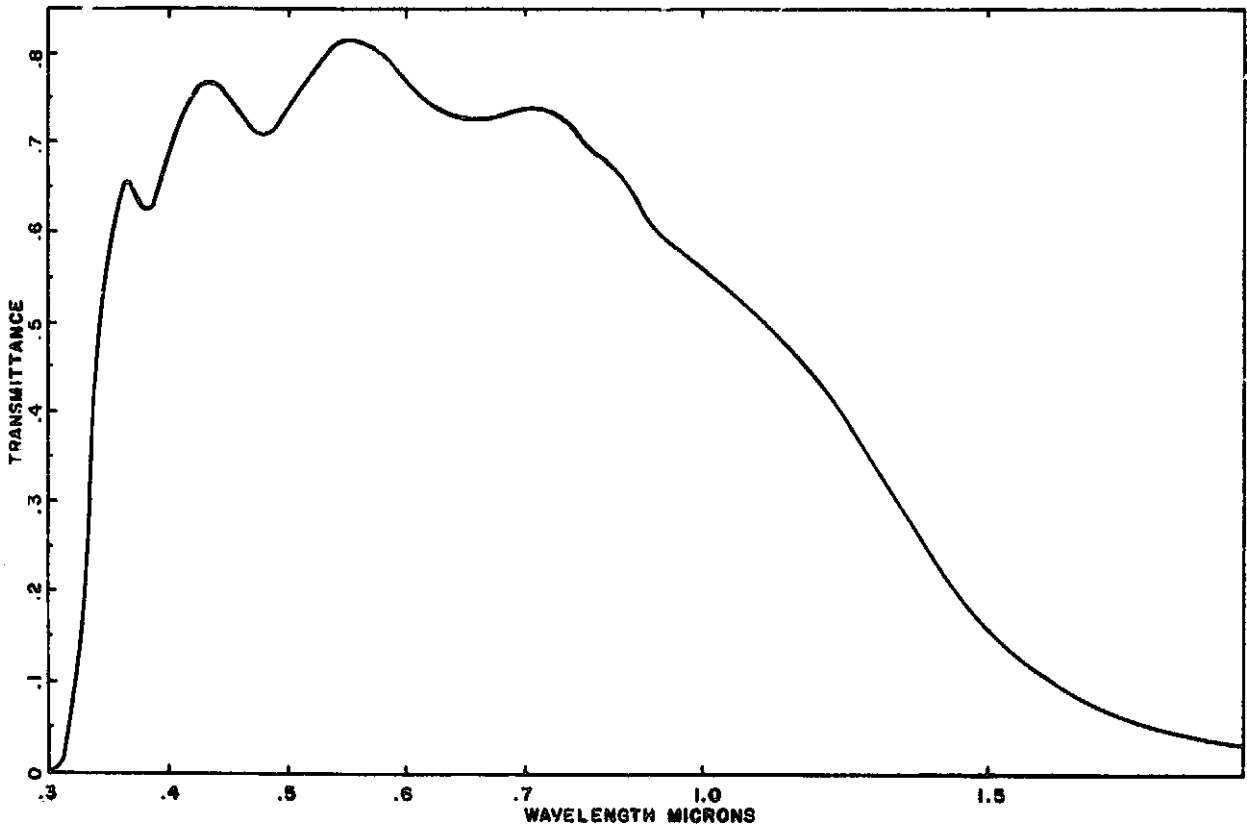


Fig. 5. Transmission of Glass - SnO<sub>x</sub> Combination

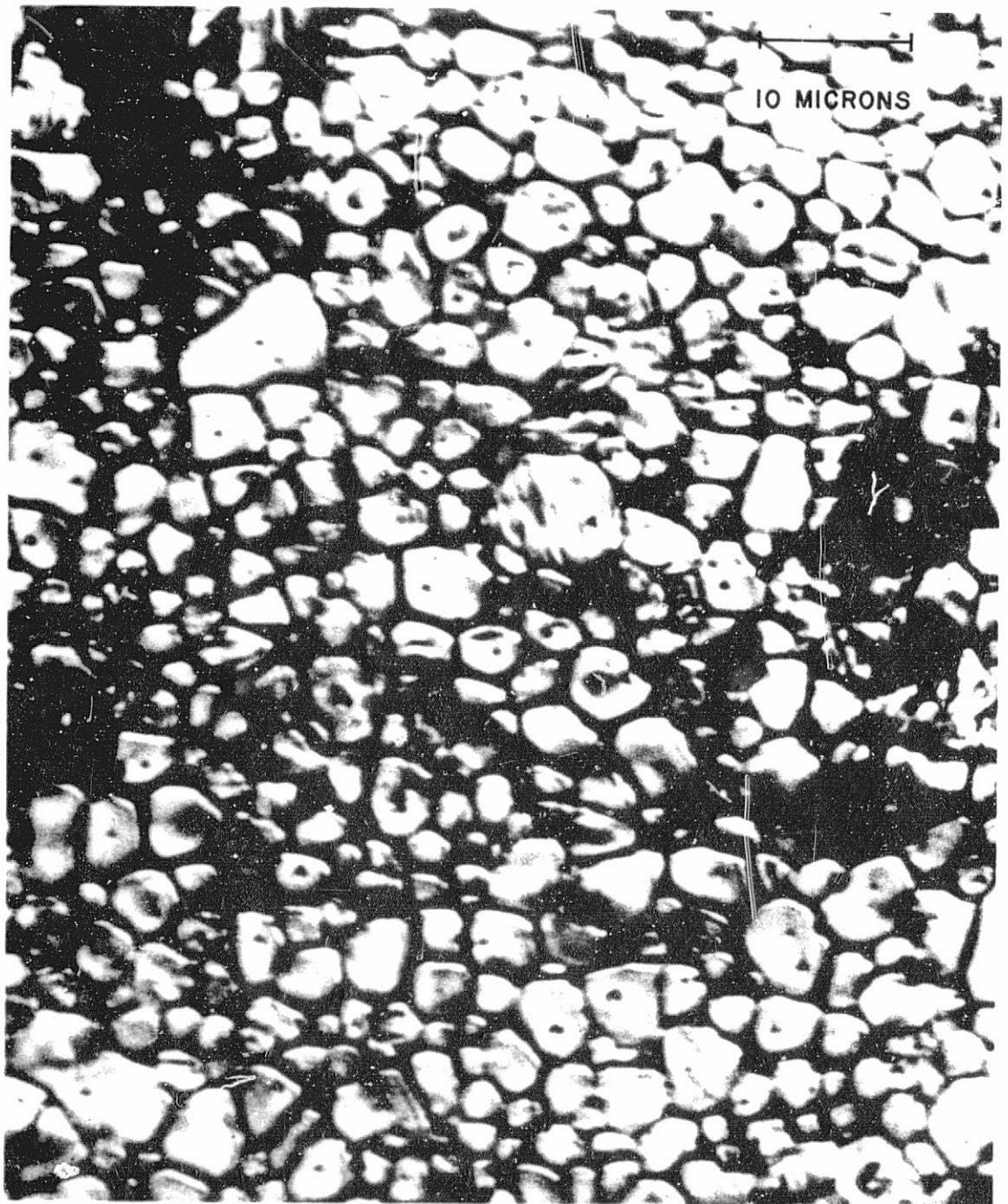


Fig. 6. Microphotograph of Crystal Film Grown by New Procedure

**SESSION V**  
**OTHER MATERIALS AND DEVICES**

## SESSION V. OTHER MATERIALS AND DEVICES

PREPARATION AND EVALUATION OF NEW II-VI HETEROJUNCTION SOLAR CELLS—  
A. Fahrenbruch and R. H. Bube

INVESTIGATION OF THIN FILM SOLAR CELLS BASED ON  $Cu_2S$  AND TERNARY  
COMPOUNDS OF THE TYPE  $CuInS_2$  AND  $CuInSe_2$  FOR LARGE SCALE TERRESTRIAL SOLAR  
ENERGY GENERATION—J. J. Loferski, et al.

THIN FILM CdTe SOLAR CELLS FOR TERRESTRIAL POWER APPLICATIONS—F. V. Wald, et al.

AN IMPROVED SCHOTTKY PHOTOVOLTAIC DIODE FOR SOLAR ENERGY CONVERSION—  
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A PROPOSED GRATING STRUCTURE SILICON SCHOTTKY-BARRIER PHOTOVOLTAIC CELL  
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GROWTH OF GaAs SINGLE CRYSTALS IN RIBBON FORM—J. B. Berkowitz\*

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ORGANIC PHOTOVOLTAIC CONVERSION—P. J. Reucroft

PHOTO GALVANIC CELLS—J. A. Eckert

ENHANCEMENT OF SELENIUM PHOTOVOLTAISM BY TREATMENT WITH PORPHYRINS—  
A. D. Adler and V. Varadi

SEMICONDUCTOR-ELECTROLYTE PHOTOVOLTAIC ENERGY CONVERTER—W. W. Anderson

CONVERSION OF SOLAR ENERGY USING PHOTOSYNTHETIC MEMBRANES—S. H. Chiang and  
G. E. Klinzing

ELECTRON-BEAM EVAPORATION OF SOLAR CELL MATERIALS—W. W. Grannemann

PIN HETEROJUNCTION SOLAR CELLS—F. Chernow

PHOTOVOLTAIC SOLAR ENERGY CONVERSION USING HIGH-TEMPERATURE THERMAL  
RESERVOIRS—I. Melngailis, et al.

PHOTO-ELECTROLYTIC DECOMPOSITION OF WATER—D. I. Tchernev

ELECTROMAGNETIC WAVE ENERGY CONVERSION RESEARCH—R. L. Bailey

VERTICAL MULTI-JUNCTION SOLAR CELLS—W. P. Rahilly

RESEARCH ON TRANSPARENT, ELECTRICALLY CONDUCTIVE MATERIAL—G. Haacke

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\*This paper replaces survey taken during NSF Workshop.

## PREPARATION AND EVALUATION OF NEW II-VI HETEROJUNCTION SOLAR CELLS

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### Presentation Summary

The purpose of Stanford's part of the NSF-RANN program is to produce and study solar cells using polycrystalline, thin film II-VI materials. Such systems are closely related to the well-known  $\text{Cu}_2\text{S}$ -CdS cell. Although the  $\text{Cu}_2\text{S}$  cell has somewhat lower efficiency than cells made from single-crystal materials, this factor is offset by the simplicity and economic advantages of using polycrystalline thin films. To overcome the stability problems arising from the high diffusivity and chemical reactivity of Cu, we propose to replace the  $\text{Cu}_2\text{S}$  layer with various II-VI compounds.

We are focusing our attention on the three heterojunction II-VI systems listed in Table I. These are the result of an analysis of possible candidates on the basis of band gap, band gap "window," the potentialities for solid solution graded junctions, and probable lattice mismatch. To these are added a fourth based on a  $\text{Bi}_x\text{S}_y$ -CdS heterojunction. The CdTe-CdS thin film cell has been studied by Bonnet and Rabinhorst (Ref. 1) who found 5-6% efficiency and good stability. Konstantinova and Kanev (Ref. 2) studied the  $\text{Bi}_x\text{S}_y$  cell and found 3-5% efficiency and good stability.

One of the major loss mechanisms in such cells is recombination through interface states formed by lattice mismatch. The  $\text{Cu}_2\text{S}$ -CdS cell shows that a 4% lattice mismatch can be tolerated if the energy barrier shape is optimized and 6-7% efficiency can still be obtained. Graded gaps can be used to further reduce the loss due to such interface states. The II-VI material combinations above can form solid solutions over the complete mixing interval (Refs. 3 and 4), thus making such graded gap heterojunctions possible.

Principal emphasis is to be placed on the p-CdTe-n-CdS system both because it is closely related to the  $\text{Cu}_2\text{S}$ -CdS system with which we have had considerable experience (Refs. 5, 6 and 7) and because its feasibility has been already demonstrated (Ref. 1).

Our experimental program is to produce such cells and study their basic characteristics in order to optimize their performance and stability. The program includes both the preparation of epitaxial films of CdTe on CdS single crystals and CdS films on single-crystal CdTe substrates. Detailed electrical and optical measurements will be made on the cells to determine dependence on preparation variables such as substrate temperature during film deposition, doping levels, and heat treatment effects. Such variables would be expected to affect both the structure of the film and the energy band profile at the interface.

Since a principal problem area is the deposition of high conductivity p-type CdTe, a number of deposition techniques are being explored. These include two source evaporation, sputtering, and a close-spaced vapor transport technique (Ref. 8). Measurements will be made of the dependences of the short-circuit current on photoexcitation wavelength and temperature, the junction capacitance dependence on bias voltage, photoexcitation and temperature, and evidence of transient effects such as optical enhancement will be sought.

Finally, similar measurements will be made on film-film cells. A second parallel exploratory program will concentrate on the other systems in Table I.

At the conclusion of the first year, results will be evaluated and the most promising avenues will be explored in greater depth. Tests for stability will then be initiated on a laboratory scale for the most promising systems.

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## Discussion

- Q: Do you have any numbers or estimates of the surface recombination velocity at the interfaces?
- A: No, I don't at this time. I have some information for the CdS-Cu<sub>2</sub>S system which I can give to you afterwards.
- Q: Do you have any results for p-type cadmium telluride yet?
- A: No, we don't. We are just set up to do that operation.
- C: The graded band gap is an interesting avenue. However, one thing is very bothersome when you grade. The graded region usually has a very much enhanced recombination probability. I would not like to discourage this, but I think if one does this, like for instance the group in Frankfort, which has done quite a bit of work on that basis, and Williams at the University of Delaware, who has done some work on that basis, major attention has to be paid specifically to the question of recombination kinetics in a graded bandgap.
- A: One comment that I have to make on that is that if we grade this junction, to a first order, the interface states are going to be of the same number, but they will be spread out over this area. So for an abrupt junction we get our profile like this and for a graded junction we might get a profile like this (drawing on the board), where the areas under these curves represent the number of interface states and the areas are pretty much constant.



Now if we spread these over this area, since the recombination through here has to involve holes in this material, we reduce the tunneling since the major loss is by a tunneling recombination process. We can thereby reduce the losses both ways.

- C: There's an additional factor if you have a solid solution of a graded bandgap material. With a statistical arrangement of the atoms of one sub-lattice, you get an additional effect for recombination.
- A: Perhaps these two could be balanced out.

Table I

Cell	$E_{g1}$	$E_{g2}$
p - CdTe - n - CdS	1.44	2.4
p - CdTe - n - ZnSe	1.44	2.7
n - CdTe - p - ZnTe	1.44	2.0
p - $\text{Bi}_x\text{S}_y$ - n - CdS	~1.5	2.4

## INVESTIGATION OF THIN FILM SOLAR CELLS BASED ON $Cu_2S$ AND TERNARY COMPOUNDS OF THE TYPE $CuInS_2$ AND $CuInSe_2$ FOR LARGE SCALE TERRESTRIAL SOLAR ENERGY GENERATION

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### Presentation Summary

#### Rationale

Presently two photovoltaic solar cells are sufficiently developed so that credible analyses can be made of their potential as the basis for large-scale terrestrial photovoltaic solar energy conversion. The single-crystal silicon cell is stable, long lived, and has an attractive efficiency but there still is some doubt about whether their price can ever be brought down low enough so that electricity produced by systems based on them will be competitive with fossil fuel or nuclear fuel generated electricity. The thin-film copper-cadmium sulfide cell promises low cost, but this cell is troubled by problems of reliability and life and has an adequate, though low, efficiency. It is therefore prudent to identify and explore other semiconductor systems that have a high potential of satisfying the requirements of long life, low cost, reliability, and acceptable efficiency.

The photovoltaic effect is very commonly encountered in semiconductors so that, in principle, every semiconductor is a candidate. However, the theory of the photovoltaic effect and certain other considerations combine to provide a filtering mechanism for selection of semiconductors on which work should be expended. The following criteria were used in selecting semiconductor systems in this program:

- (1) The forbidden energy gap should lie between 1.1 and 2.5 eV if the efficiency potential is to be comparable to that of Si.
- (2) Low cost probably means thin-film cells. Efficient thin-film cells are more likely to be made from direct gap semiconductors.
- (3) The elements comprising the semiconductors, metals, etc., used in the photovoltaic cell must be sufficiently abundant to allow manufacture of enough cells to cover thousands of square miles without encountering material-availability limits. As an indication of the level of abundance required, it would require about 4 million tons of the current variety single-crystal cell (0.008 in. thick) to generate all the electrical power needs of the U.S. in 1973. If the cells are of the thin-film type and are about  $10 \mu$  thick, the amount of semiconductor material needed would drop to about 100,000 tons. If a layer of  $1000 \text{ \AA}$  thickness is all that the cell requires, 1000 tons would be needed.
- (4) The cell should avoid the use of large amounts of very toxic substances like As, P, etc.

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- (5) The barrier can be p-n homojunction (as in silicon single-crystal cells), p-n heterojunction (as in the thin-film  $\text{Cu}_x\text{S-CdS}$  cell), or Schottky barrier (as in the  $\text{Cu}_2\text{O-Cu}$  cell). The number of semiconductors in which p-n homojunctions can be formed is limited; cells of this type have a well tested theory to fit them and could therefore be optimized more rapidly than the other more complicated types. They should also be very stable. Consequently, in selecting semiconductors for solar cells the ability to form p-n homojunctions is a desirable characteristic, but there is no a priori reason for rejecting the other kinds of junctions. Many heterojunction combinations are possible and it is therefore difficult to select compatible pairs of semiconductors. Furthermore, their theory is not very well developed so that it might be difficult to diagnose malfunctions. Metal-semiconductor cells would probably be least expensive but they could have stability problems. It seems therefore that a program aimed at new semiconductors should be open to all three types of barriers.

#### Materials Being Investigated at Brown

Based on these considerations we are engaged in an investigation of solar cells based on  $\text{Cu}_2\text{S}$  (band gap about 1.1eV),  $\text{CuInS}_2$  (band gap about 1.5eV), and  $\text{CuInSe}_2$  (band gap about 0.9eV), and  $\text{CuAlS}_2$  (band gap about 2.5eV). They are all direct gap semiconductors.  $\text{CuInS}_2$  can be made both n- and p-type; rectifying junctions have been reported in the literature for this material. Except for In, all the materials are abundant. With respect to In, if layers of the order of 1000 Å to 2000 Å thickness is all that would be needed, enough In is available.

We include  $\text{Cu}_2\text{S}$  because it is generally conceded that the 1000 to 2000 Å thick  $\text{Cu}_x\text{S}$  layer on the thin-film Cu-CdS cell is responsible for absorption of most of the solar photons and generating most of the current generated in this cell. We are engaged in finding a mate for  $\text{Cu}_2\text{S}$  other than CdS in the hope that some new combination will be more stable while retaining efficiency.  $\text{Cu}_2\text{S}$  is always p-type. The proposed barriers include metal semiconductor barriers, heterojunction barriers with n- $\text{CuInS}_2$  as one mate, and n-Si as another.

We also intend to try to make Schottky barriers to  $\text{CuInS}_2$ , as well as p-n junctions in  $\text{CuInS}_2$ .

We are proceeding as follows:

We have established cathodoluminescence as a nondestructive test for the presence of  $\text{Cu}_2\text{S}$ . We have established that of the various Cu-S compounds only chalcocite ( $\text{Cu}_2\text{S}$ ) luminesces. Other room temperature stable phases  $\text{Cu}_{1.96}\text{S}$ ,  $\text{Cu}_{1.6}\text{S}$ ,  $\text{Cu}_{1.8}\text{S}$  do not luminesce. This assertion is based on luminescence spectra observed for the  $\text{Cu}_x\text{S}$  layers formed on CdS:  $\text{Cu}_2\text{S}$  formed by converting sheets of Cu into  $\text{Cu}_2\text{S}$  in  $\text{H}_2\text{S}$  gas; chalcocite mineral specimens;  $\text{Cu}_2\text{S}$  powder synthesized in our laboratory, etc. The exact crystal structure of these various  $\text{Cu}_x\text{S}$  samples was established by x-ray powder patterns.

We attempted to form *thin* layers of  $\text{Cu}_2\text{S}$  on copper sheets by heating the copper sheet in a tube containing a known amount of  $\text{H}_2\text{S}$ . However, the films seemed to have a higher sulfur concentration at the surface than inside and were not uniform in composition.

Presently we are evaporating thin layers of Cu on Al and "sulfurizing" the Cu in flowing  $\text{H}_2\text{S}$  at temperatures between 150 and 400°C. The resulting films have been subjected to x-ray analysis, but to date they are sulfur rich, probably  $\text{Cu}_{1.6}\text{S}$ . Some of these films have exhibited cathodoluminescence characteristics of  $\text{Cu}_2\text{S}$  which suggests that there may be an extremely thin layer of the desired compound on the surface, but there is not enough of it to be detected by x-ray analysis.

We have also attempted the formation of p- $\text{Cu}_2\text{S}$  on n-Si single-crystal substrates (if it works on single-crystal Si we would shift to polycrystalline and ultimately to thin films of Si). In this case, a thin film of Cu was deposited on the n-Si and sulfurized. Since we do not yet have conditions for sulfurizing Cu into  $\text{Cu}_2\text{S}$  optimized, these experiments are necessarily in preliminary stages.

With respect to  $\text{CuInS}_2$ , the cathodoluminescence spectrum of powders synthesized in our laboratories and of single crystals grown in our laboratories have been studied extensively. The spectrum changes with sulfur content; slight departures from stoichiometry can change the conductivity and indeed shift the conductivity type. We are in the process of correlating changes in the spectrum with resistivity. Then when we make thin films of  $\text{CuInS}_2$  we will be able to determine the important semiconductor characteristics from the cathodoluminescence spectra.

**Future Plans**

Once we gain control over fabrication of  $\text{Cu}_2\text{S}$ , we will produce such layers on thin films of various metals in the hope that an acceptable metal-semiconductor cell will result. We shall continue attempts to form p-n heterojunctions between Si and  $\text{Cu}_2\text{S}$ . We have begun a program aimed at making p-n junctions in single crystals of  $\text{CuInS}_2$ . We will make thin films of  $\text{CuInS}_2$  on various metal substrates in the expectation that good Schottky barriers will be made with either n- or p- $\text{CuInS}_2$  as the basis. Next p-n junctions will be attempted in thin films of  $\text{CuInS}_2$ .

This program is in its fourth month. At Brown University it derives additional support from the NSF-sponsored Materials Research Laboratory and from an ARO grant supporting work on  $\text{CuInS}_2$  and related materials.

**Discussion**

- Q: You mentioned that most of the light is going to be absorbed in the first thousand angstroms. If the absorption coefficient at the band edge were  $10^5$  reciprocal centimeters, then 65 to 70% would be absorbed there. But I have never seen a semiconductor with an absorption coefficient at the band edge as high as  $10^5 \text{ cm}^{-1}$ . Is this the case in copper sulphide?
- A: The experimental fact is that the spectral characteristic of the thin-film CdS cell has an edge at one electron volt and that's been pretty well attributed to the copper sulphide layer, which is between one and two thousand angstroms thick for an optimum CdS cell. That's all you need.
- Q: I think the combination between copper sulphide and silicon is highly exciting because you have a very simple material there. When you go to a three-component material however, you go the other way, and so process controls become more highly complex than with a two-component substance like CdS. Questions of stoichiometry, of course, play a very important role. I notice you are looking into a sort of luminescence, and of course, this is quite sensitive. Is there some kind of feeling as to how to control the processes in order to make something which can be mass produced?
- A: Concerning the stability of these materials, the copper sulphide, as we know, is a very complicated material. But this material, the copper indium sulphide, was obtained relatively easily. And this is true of others of these I-III-VI materials.
- Q: Have you actually tried to make absorption measurements on thin films of copper sulphide? I'm thinking of absorption coefficients.
- A: No, but the coefficient of absorption beyond the edge is consistent with absorption beyond the edge, and also consistent with absorption constants of the order of  $10^5$ , between  $10^4$  and  $10^5$  reciprocal centimeters over the region of interest, the solar spectrum.
- C: As a matter of fact cadmium sulphide is, very close to the band edge, equal to  $2 \times 10^5 \text{ cm}^{-1}$ .
- A: You're right – it rises very rapidly.
- C: I would like to comment with respect to the energy gap. The energy gap in copper sulphide at 1.1 or 1.2 eV sounds rather good; but that, in fact, is the optical bandgap. Copper sulphide is a polar material and there is a Franck-Condon effect; so, in terms of thermal generation, you are stuck with a smaller bandgap, which is not quite as good. From that point of view, the cadmium telluride looks like a better material.
- Q: Well, how small a bandgap?
- A: 0.9.
- C: Okay, but if you are getting the five percent efficiency, as has been demonstrated, the copper sulphide on the cadmium sulphide substrate does give you five percent; indeed over eight percent efficiency is possible. So that should be okay.

Q: You mentioned that gallium is in limited supply; therefore, gallium arsenide photocells wouldn't be suitable for large-scale application.

A: I understand that the supply and demand fit each other, and that if one really needed the gallium it would be supplied in larger amounts. But I don't know if you can expect a tenfold increase in the production.

Q: What is the availability of indium?

A: Indium is also in short supply—about a couple hundred tons per annum, but I'm thinking in terms of a few thousand angstroms—one or two thousand angstroms of copper indium sulphide; in which case, I need something like a thousand to two thousand tons to supply all the electrical needs of the United States this year. And that kind of thing one can do with a few hundred tons per annum. The gallium arsenide cells, if they were made a few thousand angstroms thick, would be okay too.

## THIN FILM CdTe SOLAR CELLS FOR TERRESTRIAL POWER APPLICATIONS

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### Presentation Summary

The potential of CdTe for solar cell applications both at room temperature and elevated temperatures needs scarcely to be emphasized. Figure 1, which was taken from a 15-year-old report by Rappaport and coworkers (Ref. 1), makes the point for a 1.5-eV energy gap compound rather clearly; and our confidence of being able to operate CdTe at elevated temperatures has been boosted by the fact that we have designed a photoconductive near I. R. detector for 400°C operating temperatures. Such devices have now been lifetested for up to 1000 hr without degradation of any kind (Ref. 2). However, a significant effort has gone into CdTe evaporated thin film solar cells in the past; the best they have ever delivered was ~7% efficiency (without anti-reflection coatings) (Ref. 3), and they also have always shown degradation at temperatures even below 100°C (Ref. 4).

Even though the degradation of the cells can be attributed to the heterojunction technology used (Refs. 3, 4, and 5), the lack of electrical performance cannot. In particular, it is easy to estimate that irrespective of the model one accepts for the CdTe-Cu<sub>2-x</sub>Te cells; with doping levels of 10<sup>15</sup> cm<sup>-3</sup> they should deliver open-circuit voltages of ≳ 1 volt. Contrasted with this the best OCVs ever seen were between 0.5 and 0.7 volts (Refs. 3, 4, and 5), indicating a fundamental problem. A significant observation here was made by Cusano (Ref. 3), who reports that his cells, when cooled to liquid nitrogen temperature, showed OCVs of 1 volt. This observation in the context of the later work of Morehead and Mandel (Ref. 6) on electroluminescence in CdTe p-n homojunctions is very interesting. These authors observed a hundredfold increase in electroluminescent efficiency by decreasing the temperature to 77 K, and the same increase in open-circuit voltage of their junctions under illumination is evident (Fig. 2). They attribute the results to the presence of nonradiative "killer" centers near the middle of the gap and it may thus be assumed that such centers are responsible for a large part of the lack of efficiency experienced in CdTe solar cells. Although such centers might be due to native defects, Morehead already assumed them to be impurities. In our current standard material (Ref. 7) used for γ-ray detection ~10<sup>11</sup> deep centers are present per cm<sup>3</sup> as evidenced by measurements of polarization of these high resistivity (10<sup>7</sup> Ω·cm) devices (Refs. 8 and 9). In the most recent material these have been significantly reduced by subliming the CdTe before crystal growth, but workers in France have just been able to reduce the number of these centers further by only purifying the starting materials and subsequent careful handling (Refs. 10 and 11). This has resulted in γ-ray detectors which show no polarization effects whatsoever. Hence one may expect to prepare CdTe cells having much higher C/CV and thus significantly increased efficiency. This is the thrust of our proposed program as it is outlined in Fig. 3.

Since Tyco Laboratories routinely produces very high quality CdTe single crystals for both fabrication of high-temperature fire detectors and γ-ray detection devices, we propose initially to produce homojunction solar cells using single-crystal wafers. It is to be emphasized, however, that single-crystal cells do not constitute the main thrust of the program; their production is considered valuable, however, since such cells can be used to give information on the maximum efficiency obtainable with CdTe as well as providing data on the dependence of this efficiency on temperature.

To start, single-crystal CdTe will be grown, doped both p and n-type with various suitable selected dopants. Concurrently, epitaxial deposition experiments will be carried out using either liquid or vapor phase epitaxy methods to deposit various thicknesses of oppositely doped top layers on single-crystal CdTe substrates. Characterization

of both the single crystals and the junctions grown will then be carried out. Since for all electrical characterization, good contacting techniques are a necessity anyway, contacting metals and methods will also be studied in this phase. As the first milestone, the junctions made will be evaluated in the form of small ( $1 \text{ cm}^2$ ) solar cells and their efficiency will be measured versus temperature.

Having now arrived at the proper choice of structure via the single-crystal route, we are, of course, faced with the problem of transferring this structure onto a suitable substrate film; the choice of substrates is governed by both economic/operating constraints and preparative ones. The first question here would be whether one is talking about extremely large cell areas operating near room temperature or a suitable smaller area cell for topping purposes which has to operate at elevated temperatures. Other constraints are set by factors such as the deposition temperature and the contacting metal. In any event, a prudent general statement seems to be that plastic substrates will probably be the cheapest — after all, polyimide films are available which tolerate temperatures up to  $400^\circ\text{C}$ , which will certainly cover any envisioned operating range for CdTe cells. On the other hand, to obtain reasonable grain sizes in the films may necessitate high temperatures in the deposition step, and organic substrates may no longer be usable, in which case metals have to be used. Metallic substrates, however, must be chosen such that they can also form a contact to CdTe or at least be metallurgically compatible with a contacting metal at the deposition temperature. Furthermore, metal substrates must be cheap, and we believe that practically any metal foil, except for iron and aluminum, may have to be excluded on economic grounds.

Faced with all this complexity, we propose as a first step the use of sapphire substrates to establish initial vapor deposition methods and their operating parameters. This substrate offers a number of advantages for initial investigation. Firstly, it offers a single-crystal surface compatible with virtually any contacting metal one might imagine for the temperature range involved in the deposition study. Secondly, it has no problems of thermal decomposition, evaporation, melting, and the like. Thirdly, it is insulating and transparent and would thus more easily allow the study of films deposited. Finally, EFG grown sapphire substrates are readily available at Tyco and, parenthetically, they might eventually be cheap enough to be an economically viable choice as a substrate for a terrestrial cell, most certainly for a topping-type elevated temperature cell. In any event, sapphire seems to be an almost ideal choice for study purposes to establish a thermodynamic and kinetic baseline for the deposition of CdTe.

After having established deposition parameters, such as temperatures, partial pressures, and the like, as well as the compatibility between CdTe and the base contact, one must, however, proceed to the somewhat messy area of selecting a real world cheap substrate. So far as the situation presents itself now, the choices range from metallized "Mylar" and "Kapton" (polyimide) films to transformer iron. Transformer iron is mentioned here since it is both cheap and can be made with larger grains of highly preferred orientation. Thus, deposition experiments must be made on the basis of time and effort available. But more important here is inventiveness in arriving at economically feasible choices of substrates which also meet the technical criteria of cell operating temperature and compatibility with the contact metal in a metallurgical sense, as well as the deposition method in the processing sense.

Finally, a few comments on the economics and availability of the raw materials. Cadmium at present is \$20/lb in semiconductor purity, Te \$30. As for availability the question certainly turns on Te and not Cd. Tellurium, which has few uses at present, is recovered mainly as a byproduct of Cu refining where, according to one estimate (Ref. 12),  $> 95\%$  of it is lost before it gets recovered. At present, annual production in North America is 100-150 metric tons and the production of the rest of the world is  $\sim 140$ -180 metric tons with much fluctuation. It seems that with some ease 500 tons of Te annually could be made available by one North American manufacturer alone at a notice of 3 years (Ref. 13) and world production certainly could exceed 1000 tons/year from present recovery schemes alone. Tellurium is easy to remove and refine, which accounts for its current low price in high purity form and although it will not ever be basically as available as silicon or sulphur, there is enough to add something like  $5 \cdot 10^{10} \text{ kWh/year}$  of direct solar energy generating capacity per year based on the current supply route. This assumes a  $10 \mu$  thick, 10% efficient cell with 5:1 concentration of sunlight. All in all we believe that to be a worst case estimate for the Te supply, but consider it to be a near optimum estimate for conversion technology in so far as minimization of CdTe use is concerned.

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## Discussion

- Q: Have you further information on the diffusivities in cadmium telluride? There has been some question of stability of cells of this kind. When you go from the sulphides to the selenides to the tellurides, usually the diffusivity increases as the binding energy of the lattice increases. Have you had some ideas of what it is?
- A: Yes, we have a rather large body of experience from this 400°C photodetector. Metals which you can use as contacts to cadmium telluride at elevated temperatures are few and far between. I mean you can diffuse silver at 500°C through five millimeters of cadmium telluride in half an hour. This is simply seen by viewing the cadmium telluride by transmitted infrared light after depositing silver on one side and heating it. It gets black in half an hour. However, the dangerous metals in this respect are, in the main, copper, silver, and gold, and I believe, for a homojunction solar cell anyway, copper. These are species which must be strictly excluded because they form relatively deep states, and they will form rather strong electron traps as soon as one drops the Fermi level below them in p-type material. So there are rather dangerous dopants in the cadmium telluride for solar cell purposes, I would say. So they have to go. On the other hand, there was a variety of materials which we found that didn't diffuse very fast: nickel, molybdenum, rhodium, and tin. We finally chose molybdenum for the photodetector for reasons other than for diffusion. I don't think there is a problem with diffusion if one watches those species which are prone to diffuse -- mostly by some coupled process by forming vacancies for the same kind, and so on and so forth. I think that is something which is now very well understood.



- C: As you probably know, Radio-Technique in France has been making cadmium telluride cells for several years.
- A: Yes.
- C: But the major problem that I have heard about is the stability of the cells under humidity.
- A: Now they have made only homojunction cells. I cannot address myself to the cuprous telluride film as to what goes on there. I am just thinking of trying to make heterojunctions. We have here all these combinations with p-type cadmium telluride, and no homojunction is proposed.

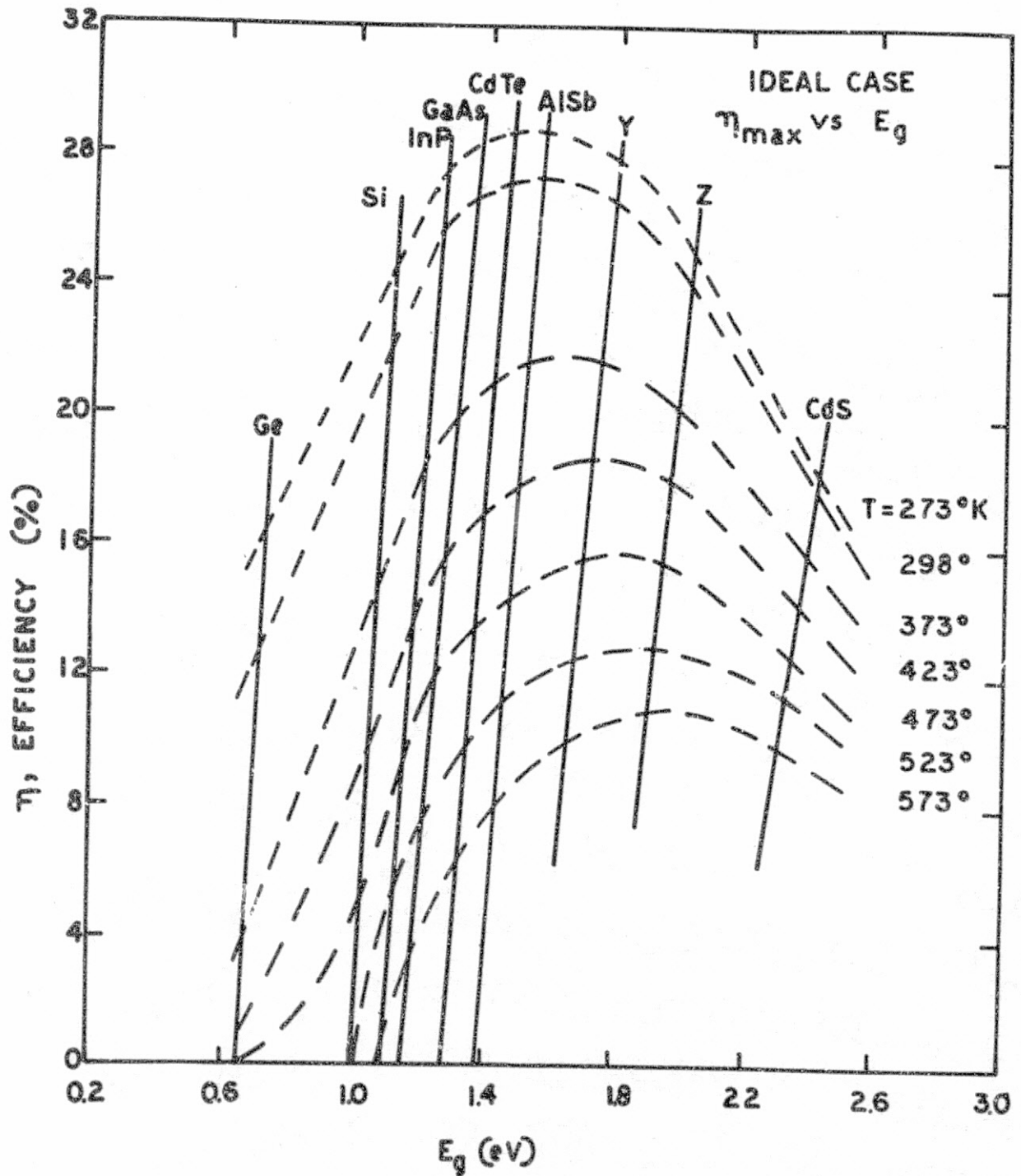


Fig. 1. Theoretical Solar Cell Efficiency for Selected Semiconductors as a Function of Temperature (After Rappaport, Ref. 1)

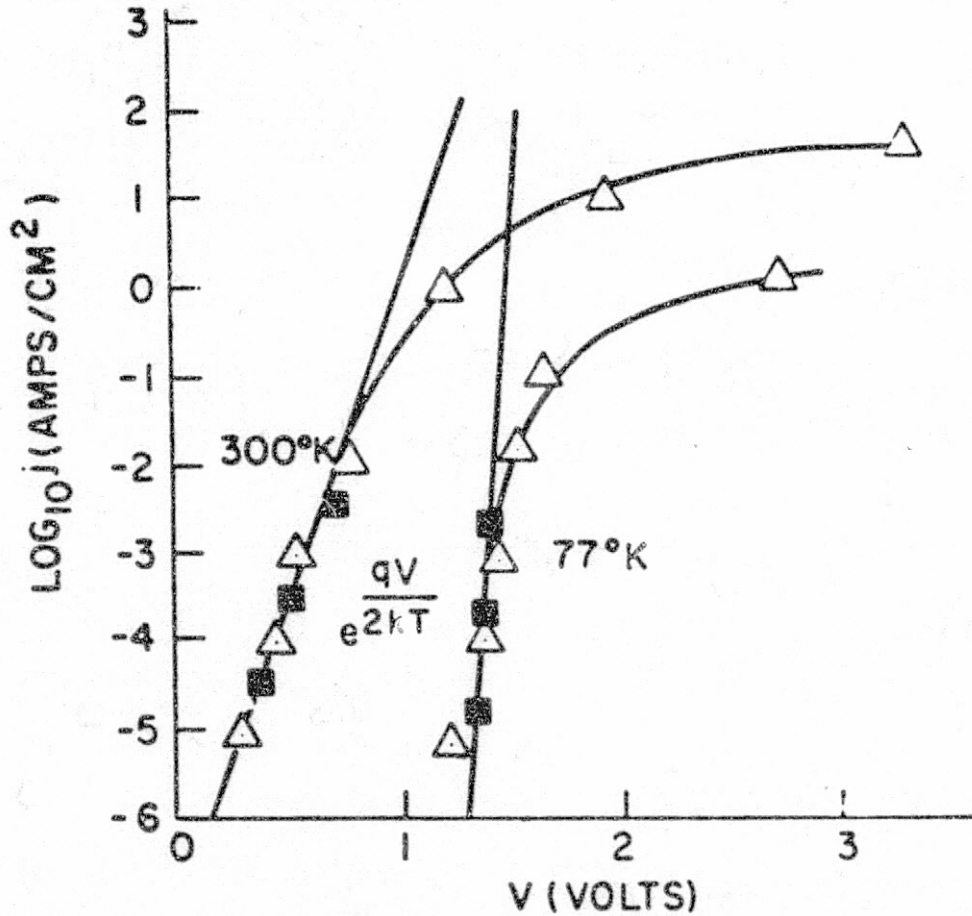
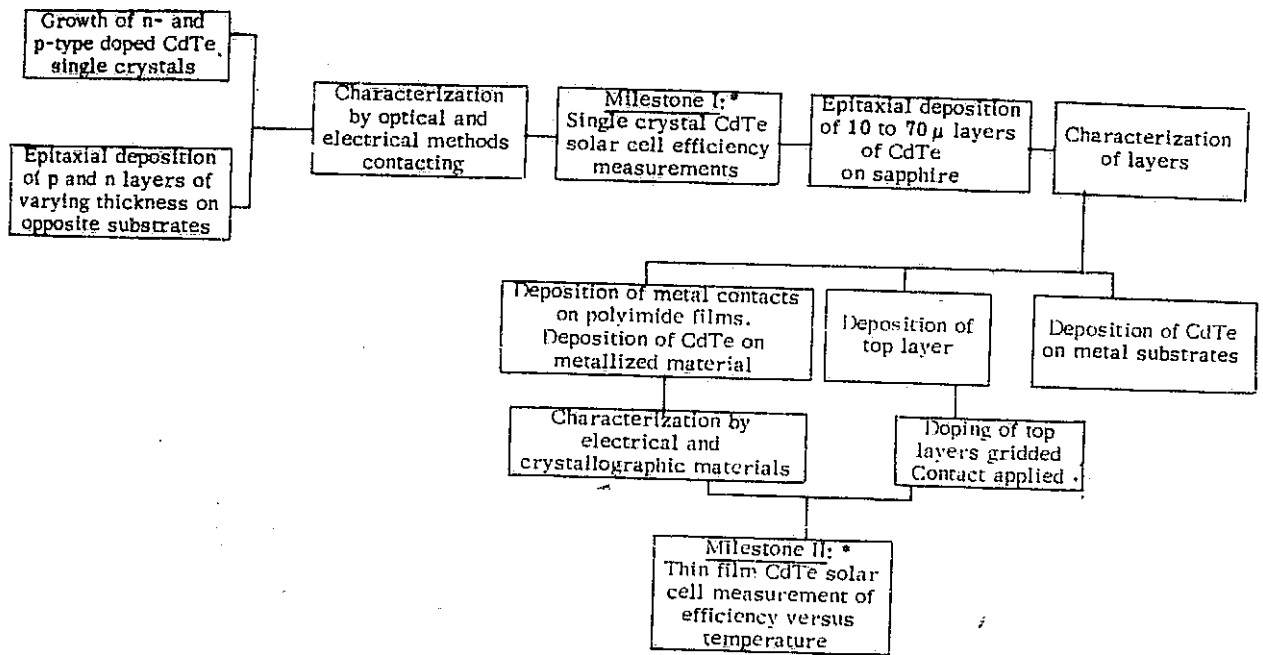


Fig. 2. A plot of the photovoltaic and current-voltage data for CdTe diffused diodes at 77 and 300°K.  $\Delta$  = the current density through the diode vs the voltage applied at the diode contacts.  $\blacksquare$  = the short-circuit current density produced by illumination of the diode junction vs the open-circuit voltage for the same level of illumination. At currents  $< 10^{-3}$  A  $\text{cm}^{-2}$ , the j-V data and the photovoltaic data both follow the  $\exp(qV/2kT)$  voltage dependence, indicating control of the current by recombination in the space charge region. At higher currents the j-V characteristics are dominated by the high series resistances in the diode (contacts, etc). (After Morehead, Ref. 6).



\* Each milestone reflects a time span of one calendar year.

Fig. 3. Flow Sheet of Proposed Program

## AN IMPROVED SCHOTTKY PHOTOVOLTAIC DIODE FOR SOLAR ENERGY CONVERSION

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### Presentation Summary

#### Research Summary

A study of Schottky barrier diodes on p-type silicon for solar energy conversion has been underway at Rutgers for 18 months. The purpose of this research is to study materials and techniques of fabrication to permit construction of a photovoltaic energy converter having a low cost per kilowatt and high efficiency (>10%) for practical terrestrial applications. The study involves device technology, vacuum deposition techniques, optical design optimization, electrical design optimization, and studies of metal alloys.

Figure 1 shows the device structure used in the initial work (Ref. 1). The semitransparent metal layer permits passage of solar energy and forms the depletion region in the semiconductor for collection of generated carriers. The carriers are generated by conversion of photon energy to electron-hole pairs. A computer solution (Ref. 2) of the optical problem shown in Fig. 2 has been made to determine the parameters which maximize transmission ( $T_0$ ) and minimize reflection ( $R_0$ ). Table I shows that a  $TiO_2$  antireflection coating can increase  $T_0$  from 24.7% to 56.7% at a wavelength of 6000 Å using a 100-Å Cr barrier metal. Table II shows results of the computer analysis for a thin film device consisting of air-thin Si-thick Cr ohmic contact. The Si forms its own antireflection coating when it has the proper thickness (1845 Å). The proper Si thickness maximizes absorption in the Si by establishing a constructive phase relationship between successive transmitted and reflected waves.

A more exact analysis results by using

$$J = C \left[ \frac{\sum_{\lambda} w_{\lambda} T_{\lambda} I_{\lambda} f_{\lambda}}{\sum_{\lambda} w_{\lambda}} \right] \quad (1)$$

where  $T$  = transmittance into silicon,  $I$  = solar intensity spectrum,  $f$  = quantum efficiency, and  $w_{\lambda}$  = a mathematical weighting factor to account for sampling unequal wavelength intervals. This predicts that a 520-Å coating of  $TiO_2$  will increase short-circuit current density by 87% in a Schottky diode having a 100-Å Cr barrier metal. A 680-Å layer of  $SiO_2$  should increase current density by 77%. Experimental data on diode 67 are given in Table III. This shows a 560-Å coating of  $SiO_2$  to increase current density by 40% and efficiency by 50%. It is also shown that true solar illumination gives a better response than does the tungsten lamp. This improved efficiency is still not optimum because of the improper thickness of both barrier metal and oxide coating.

A study of solar cell resistance begins by an examination of Fig. 3. This shows that much of the active diode area does not contribute to useful current generation because this large area device does not possess current collecting fingers shown in Fig. 4. This problem can be solved through proper finger design and use of barrier metal having a greater thickness or conductivity. A further study of this problem produced data shown in Table IV. A figure of merit for the metal is defined as the ratio of transmittance ( $T$ ) to resistance ( $R$ ). The best film should have a high transmittance and a low resistance. The poorest performance is shown by evaporated Cr. The best performance

was obtained on sputtered Cu/Cr alloy. This shows that sputtering and alloying can be used to improve on the figure of merit for thin metal films. But other problems arise which prohibit the simple application of this analysis of thin metal films.

Figure 5 shows the I-V characteristic for diode number 77 having a  $0.04\text{-cm}^2$  area and  $540\text{-\AA}$  Cr barrier metal with  $100\text{-mW/cm}^2$  tungsten lamp illumination. This device exhibits a 7.5% efficiency which is less than the 15% theoretical figure (Ref. 3) due in part to the lack of an antireflection coating. A  $1.5\text{-cm}^2$  device with current collecting fingers has exhibited a 3% efficiency. This will improve with more work in the area of contact design, metal selection, and antireflection coatings. The transition metals Nb and Mo have also been observed to permit good photovoltaic response in p-type silicon. Platinum should also be a good candidate because it exhibits a transition metal band structure similar to Cr, Mo, and Nb. Sputtered diodes exhibit a low open-circuit voltage due to the penetration of sputtered atoms into the Si resulting in barrier modification. Problems, proposed solutions, and program goals are defined below as a result of this research. Our new evaporation equipment will permit us to explore most of the proposed solutions.

#### EXISTING PROBLEM/Proposed Solution

**EVAPORATED FILMS HAVE HIGH RESISTANCE AND LOW  $T/R$ .** Substrate heating to mobilize atoms during deposition. Use of alloys by co-deposition. Electron beam deposition. Monitor film resistance during deposition.

**SPUTTERED DIODES HAVE LOW OPEN-CIRCUIT VOLTAGE.** Reduce sputtering voltage. Evaluate alloy metals from sputtering tests, then use evaporation to fabricate diodes.

**ANTIREFLECTION COATINGS HAVE NOT YET IMPROVED PERFORMANCE AS MUCH AS PREDICTED.** Precisely control film thickness by monitoring film thickness during deposition.

**EFFICIENCY IS LESS THAN THE THEORETICAL VALUE.** Improve  $T/R$  using alloys and substrate heating. Improved antireflection coatings. Modified contact design. Full device fabrication with one pump-down of the vacuum system.

#### Program Goals

- (1) Increase the efficiency of small area ( $<0.1\text{ cm}^2$ ) Schottky diodes to 15% (presently 7.5%).
- (2) Increase the efficiency of large area ( $>1\text{ cm}^2$ ) diodes to that of small area ones (presently 3% for the large area diode).
- (3) More fully evaluate other metals and alloys as barrier metal candidates.
- (4) Explore the use of Schottky barriers on thin-film ( $<1\mu$ ) semiconductors.

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## Discussion

- Q: I would like to make several comments on the discussion of the optical properties of the metals. I feel that too much emphasis is being placed on that since the dielectric constants of the metal in that range of thickness are very thickness-dependent. Varying the metal alloy composition would be a minor effect as compared to the strong thickness dependence. Thus, any calculations you make have to take into account the actual dielectric constants, which are very difficult to obtain. Secondly, you mentioned getting high film resistance -- this is more a problem of the surface. I think you will find that the smoother the surface that you are putting the film on, the lower this resistance will be. This is due to the aggregate nature of the film. Thirdly, I noticed that your fill factors are quite low. It is actually quite easy to get a high fill factor with a Schottky barrier. This is because of the absence of diode leakage currents, and, hence, A-factors more nearly equal to unity. I suspect that you are having problems with very thick interfacial layers. This also could be the reason why the larger areas are less efficient than the small areas as well as, perhaps, the high series resistance. Lastly, I would like to ask why you believe the Schottky barrier approach on silicon is worthwhile, given the fact that light is not absorbed strongly in silicon?
- A: I will try to cover all of these areas. First of all the values of  $N$  and  $K$ , the optical properties, as a function of thickness have been known, and we are determining these properties at the present time by depositing films of various thicknesses and measuring  $R$  and  $T$  effects on transmission and then calculating  $N$  and  $K$ . These have been worked on.
- Q: Would that be on glass substrates?
- A: That's correct. We are correcting for the presence of the glass to the metal. The last diode we made was made with equipment monitoring the resistance of the film, and we found a significant improvement in the device characteristics by just making sure the resistance of the film is of the proper value. So this has been looked at. Thirdly, the interfacial problem can be solved by fabricating the entire device with one pump-down of the vacuum system. At the present time we cannot do this, but with our new equipment we are going to be able to make the entire device with one pump-down, using substrate heating and multiple-source evaporation. We think this will improve the interface problem. In response to the last question, Schottky barriers have a great flexibility in choice of materials -- an infinite number of metals and alloys and many different semiconductors. It's a very good process. Once you have your semiconductor, you simply pass it through your vacuum system and you can simultaneously obtain not only the contact but the Schottky barrier at the same time.
- Q: I am not questioning the Schottky barrier approach, but rather the choice of silicon.
- A: Why silicon?
- Q: We know that the voltage output must be less than that obtained from junction-type devices. Let's say you want to make up the loss somewhere else -- the only other place is in the current. But in silicon most of the generation is some distance away from the barrier. So how does the Schottky barrier improve things?
- A: I chose the Schottky barrier because of its simplicity, and I chose silicon because it is so plentiful and so much is known about silicon. I feel that with the thin-film device you can make a Schottky barrier diode on silicon with the silicon thickness of the order of 2,000 angstroms. This occurs because of the fact that with the proper silicon thickness, it forms its own antireflection coating and you obtain multiple passes of the radiation through the silicon. The radiation passes into the silicon, is bounced off the interfacial layers, and you can get constructive interference.
- Q: At one wavelength?
- A: This can be designed to occur at the most important wavelength, which is 6,000 angstroms.
- Q: Could you explain the effects from sputtering the metal?
- A: Yes. Your sputtered atoms leave the target material with a finite velocity, and they then penetrate a short distance into the silicon. Because of this, you don't have a true Schottky barrier that will obey the

- fundamental laws. We have measured I-V characteristics and C-V characteristics that show that the sputtered diodes do not. It is just due to the fact that the ions probably penetrate into the silicon.
- Q: Presumably they are not ions? They are neutral atoms and average about 10 eV?
- A: Yes. Well, no, the ions which strike the target are accelerated at from two to five keV.
- Q: You are talking about the specularly reflected?
- A: Right. The atoms which leave the target metal leave with a finite velocity and there is a profile of this velocity.
- Q: I would like to ask you several questions. One is that you used metal film thicknesses within about a hundred angstroms. Is there a reason for that? Have you tried thinner metal films and so on?
- A: A problem with the metal films is that if they are too thin they are not continuous, and then you have a very high resistance. I am not even sure now that a hundred angstroms is the best value.
- Q: That then relates to the second question. How do you prepare your surfaces? We have been working with Schottky barriers with different thicknesses for electroreflectance measurements on silicon and on gallium arsenide. I have personally made very good measurements of Schottky barriers with metal-film thicknesses of 40 angstroms, and got very good electrical reflectance with very good electrical continuity. So you have to have good preparation of the surface as was remarked on earlier.
- A: The surfaces are very smooth. The silicon has been finely etched and polished.
- Q: How do you do this?
- A: They are purchased from outside vendors.
- Q: Then you don't really know what the quality of the surface is?
- A: If you take a look at it under the microscope, it looks flawless. Also, we studied a number of different films using the electron microscope, and we've shown very clearly that if you get down below 50 angstroms, you are not going to have a continuous film.
- C: I should comment that this is a power device and you really have to consider series resistance. You did not have to consider series resistance, whereas the solar cell is a power device and is handling much more current. So there is quite a difference between the two applications.
- C: Yes. I realize that point. It's just that electrical continuity still seems to be there at about 40 angstroms.
- A: We measure the film resistance as a function of time while the sample is being evaporated, and the thing is definitely an open circuit until you get to a certain thickness. There is just no question about it.
- Q: What is the size of your device?
- A: We are working with samples which are a few millimeters by a few millimeters; but that is only because that's all we need in order to focus our light on them. We have made them on things on the order of half a centimeter by half a centimeter.
- Q: Your current-voltage characteristic, which shows a relatively small fill factor, has the typical sign of a series resistance limitation. You have a horizontal branch and then it goes with a rather shallow slope that seems to indicate that even 100 angstroms is too thin and not too thick. That seems to, for this particular kind of device, speak against making it even thinner. Wouldn't that suggest that you should possibly go to a somewhat thicker layer rather than thinner?
- A: Yes, and also the use of alloys should help considerably in the resistance.
- Q: You had a curve showing current characteristics as you opened your sample to the light, and when you got near the contact, did it level off?



- A: No, it was going the other way. We started near the contact and then we went away from the contact and it leveled off as we got farther away.
- C: We have a grant at Brown supported by NASA in which we are looking at, well ultimately, metal-semiconductor barriers on silicon. There is a way of increasing the transmission while decreasing the resistance, and that is to gather the metal together into stripes on the surface. The stripes could be separated by a diffusion length, so 10 percent of the surface may be covered by such stripes. So you lose 10 percent, but that's still lower than the 30 or 40 percent that you give up by covering the whole surface. So, that is another approach.
- A: Yes. We have considered this.
- C: But then you don't get a depletion region everywhere. Also, not nearly that much is lost by absorption.
- C: Provided that the stripes are less than a diffusion length apart, you don't need to have a depletion region.
- C: I don't agree -- current collection will be reduced. Collection should be field-aided as much as possible.

Table I. Solution of the Four-Layer Optical Problem (Ref. 2)

Dielectric Type	Dielectric Thickness (Å)	Dielectric Constant (n)	Reflection from Front Surface (%)	Transmission into Silicon (%)
TiO <sub>2</sub>	505	2.	2.2	56.7
Si	260	3.72	9.1	45.0
SiO	720	1.8	15.7	48.9
MgF <sub>2</sub>	975	1.38	34.7	37.9
None	—	—	57.5	24.7

Air-dielectric-100 Å Cr-silicon at  $\lambda = 0.6 \mu$ .

Table II. Solution of the Thin Film Device Problem (Ref. 2)

Silicon Thickness (Å)	Reflection from Silicon (%)	Transmission into Cr (%)	Absorption in Silicon (%)
240	1.2	74.8	24.0
1045	5.1	43.4	51.5
1845	11.4	27.3	61.3

Air – silicon – Cr at  $\lambda = 0.6 \mu$ .

Table III. Antireflection Coating Study

Dielectric	(a) None	(a) SiO(560Å)	(b) SiO(560Å)
$V_{oc}$ (V)	0.43	0.44	0.41
$I_{sc}$ (mA)	10.2	14.0	17.0
$I_{max}$ (mA)	10.2	15.0	--
$P_{max}$ (mW/cm <sup>2</sup> )	2.93	4.4	--
$P$ (mW/cm <sup>2</sup> )	1.76	2.64	2.79

Diode 67 with area = 1.5 cm<sup>2</sup>

120-Å Cr film with 48% transmission and 7330 Ω/□

(a) = using 100 mW/cm<sup>2</sup> tungsten lamp

(b) = using hazy sunlight

$V_{oc}$  = open-circuit voltage

$I_{sc}$  = short-circuit photo-current

$I_{max}$  = maximum photo-current

$P_{max}$  =  $I_{max} V_{oc}/A$

$P$  =  $I_{sc} V_{oc}$  (Curve Factor)/A

Table IV. A Study of Thin Metal Films

Sample	Metal	Deposition	Thickness (Å)	R Resistance ( $\Omega/\square$ )	T Transmission (%@0.6 $\mu$ )	T/R Quality
69	Cr	Evap.	325	1650	64	0.039
77	Cr	Evap.	540	1200	40	0.033
78	Cr	Evap.	—	715	32	0.045
79	Cr	Evap.	—	755	39	0.051
81	Cr	Evap.	350	630	31	0.049
68	Cr	Sput@2.5 kV	245	315	33	0.105
70	Cr	Sput@2.5 kV	115	355	38	0.107
75	Cu/Cr	Sput	100	340	57	0.168
80	Cu/Cr	Sput	100	350	57	0.163

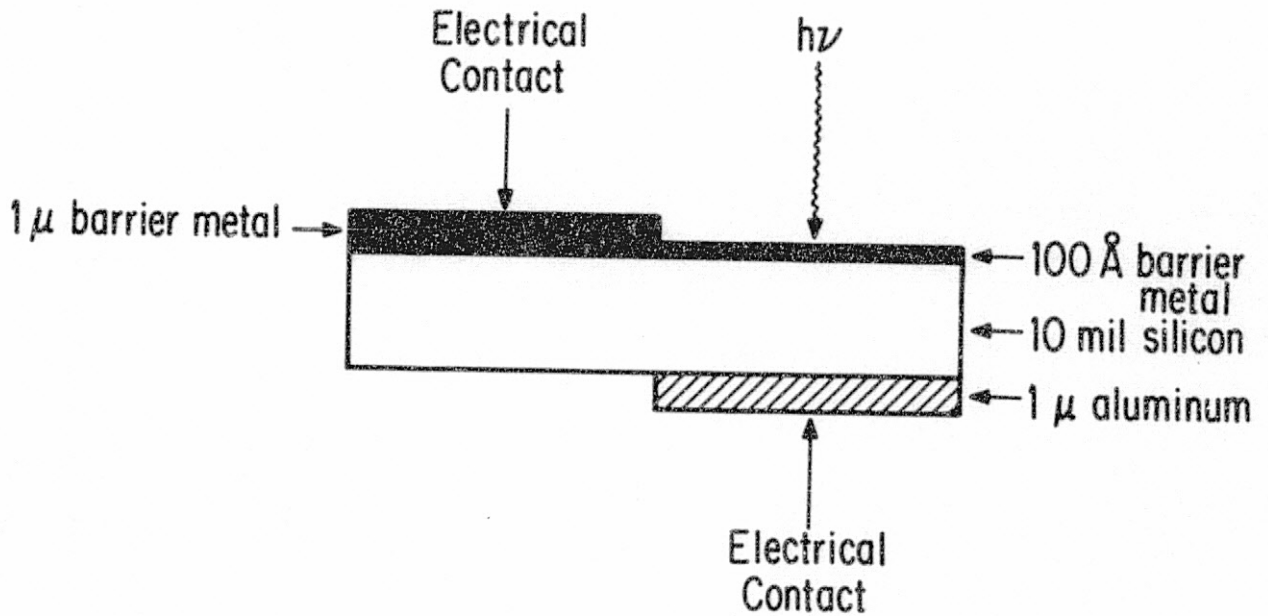


Fig. 1. Structure for a Schottky Solar Cell

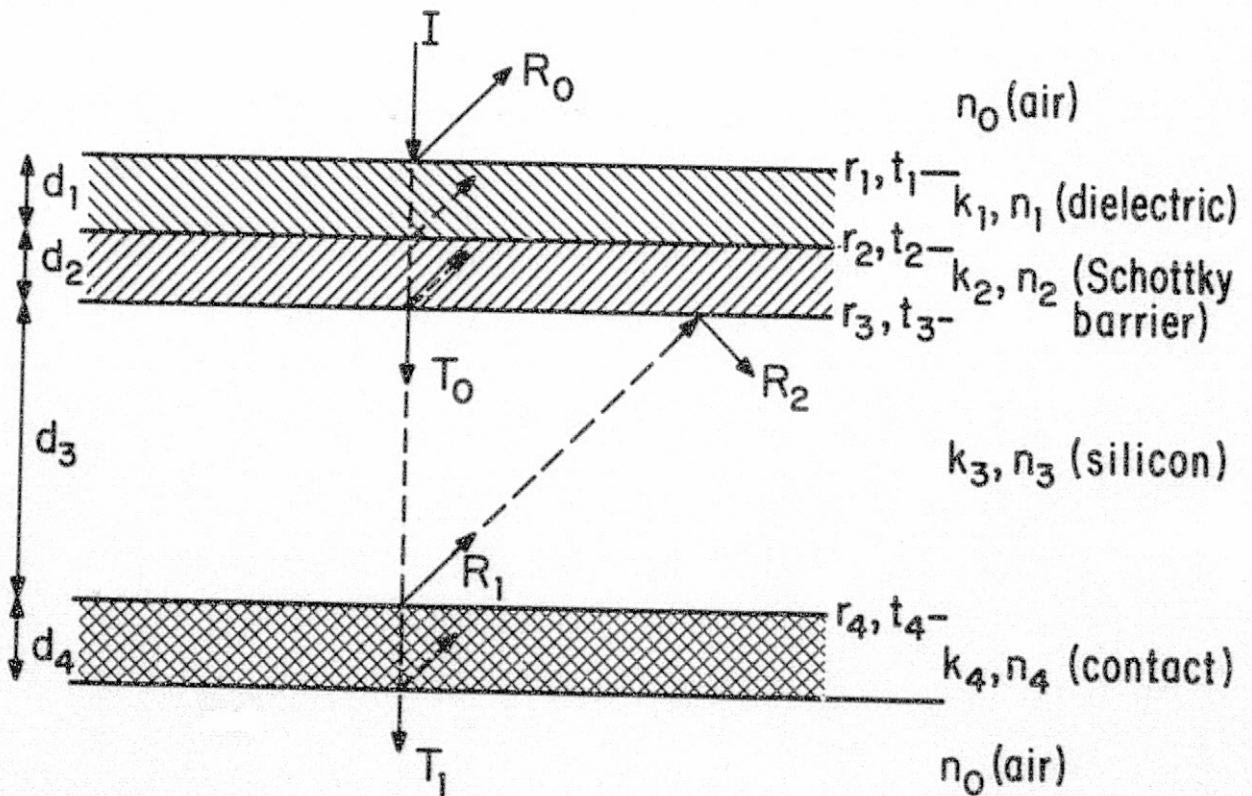


Fig. 2. Optical Configuration for a Schottky Solar Cell

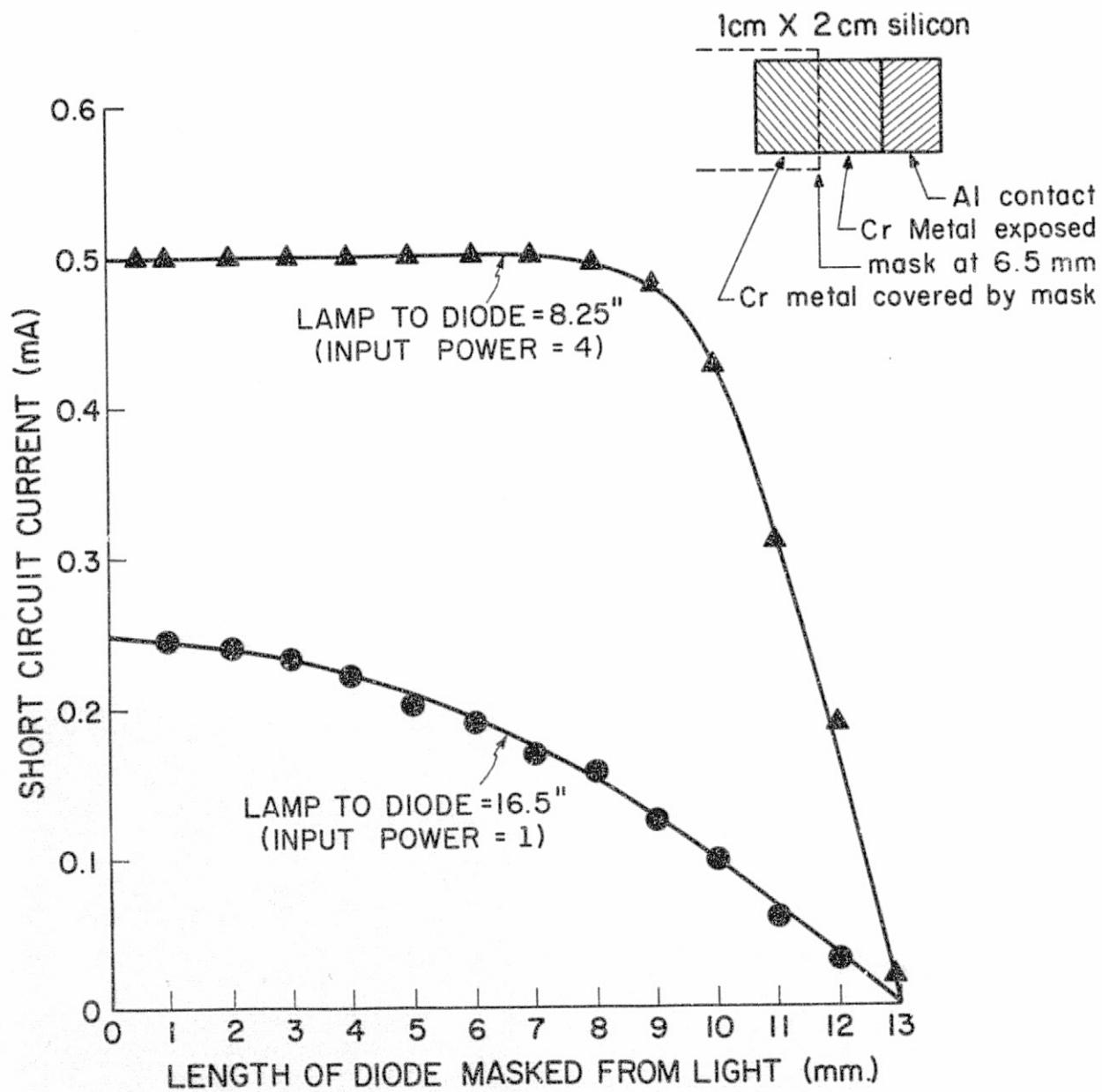


Fig. 3. Power Loss Caused by Poor Contact Design

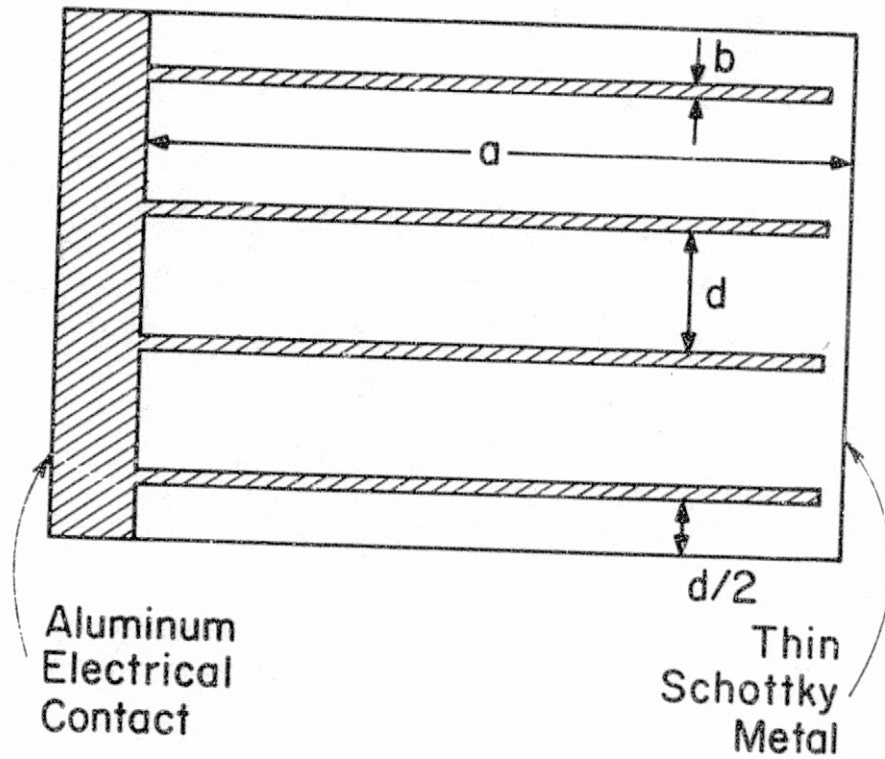
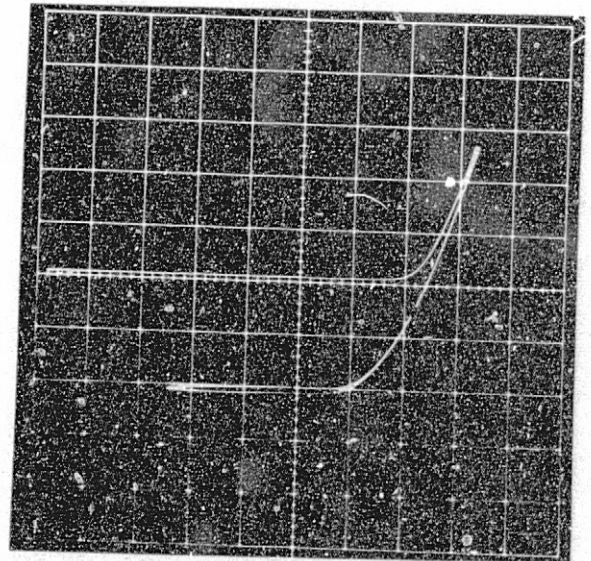


Fig. 4. Electrical Contact for a Schottky Solar Cell

Fig. 5. I-V Characteristic for Diode 77. Upper Curve Is Without Illumination. Lower Curve Is With 100 mW/cm<sup>2</sup> Tungsten Lamp Illumination. Horizontal Scale = 0.2 V/div. Vertical Scale = 12.5 mA/cm<sup>2</sup>/div. Efficiency = 7.5%



## A PROPOSED GRATING STRUCTURE SILICON SCHOTTKY-BARRIER PHOTOVOLTAIC CELL FOR SOLAR ENERGY CONVERSION

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### Presentation Summary

We propose here a new grating-type silicon Schottky-barrier photovoltaic cell for solar energy conversion. The idea is based on our recent development of a high sensitivity and broad-spectral response grating-type silicon Schottky-barrier photodetector (Ref. 1). Our objective is to design and fabricate research samples of the above proposed cells that would potentially yield an overall conversion efficiency exceeding the 10–13% of present silicon p-n junction cells while simultaneously reducing the manufacturing cost substantially. Our proposed solar cells could thus be used economically for large scale terrestrial applications of the photovoltaic systems. The specific cell's design (layout, geometry, and structure) for achieving the above goals are illustrated in Figs. 1, 2, and 3. Figure 1 shows a schematic representation of a grating structure cell and its energy conversion scheme. Figure 2 displays a typical design of a grating-type silicon Schottky-barrier photovoltaic cell with rectangular geometry. Figure 3 shows some design morphology of grating structure cells, discrete or integrated.

Unique features of our proposed cell's design include: (1) metal grids replace the conventional thin metal-film ( $\sim 100 \text{ \AA}$ ) and the ZnS antireflection coating; (2) the device can be readily constructed by employing standard silicon planar technology, with fewer processing steps required than the conventional silicon p-n diodes; (3) no high-temperature diffusion process is needed in device fabrication; (4) our proposed cells have a better solar spectral-matching ability than silicon p-n junction cells and thus higher conversion efficiency is expected for our cells; and (5) our proposed structure is simple and potentially suitable for mass production in a pilot line, as a single cell or as integrated solar arrays, thus the cost could be further reduced.

Our initial calculation indicates an overall conversion efficiency of 16–21% and an output power of 18–23 mW/cm<sup>2</sup>, depending on the operating temperature of the cell, could be achieved by our grating-type silicon Schottky-barrier photovoltaic cells.

Our immediate research goal is to construct research samples by using different metals or metal-alloys (e.g., Au, Au-Cr, Al, and Pd) evaporated or sputtered on single-crystal silicon substrate and studying their contact properties as well as their performance characteristics. Optimization of cell designs will be made with respect to the grating spacing, surface-layer doping density, and the reflection loss. To further reduce the cell's overall cost, we plan to construct grating-type Schottky-barrier cells by using polycrystalline silicon films as substrates. The characteristics of such cells will also be measured and analyzed.

Our cell's fabrication and analysis will be carried out at the Microelectronics Laboratory of the Department of Electrical Engineering of the University of Florida, where excellent in situ research facilities exist for integrated circuits and semiconductor device fabrication.

### Reference

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## Discussion

- C: We have been making grating cells of various types of p/n junction grating cells, most recently involving aluminum, which is then alloyed in at the eutectic temperature. We find that quantum yields are near unity at the limits of what we can measure -- 3500 angstroms or so. There is this recurring question from Dr. Stim about why Schottky barriers on silicon. The thing that is needed in that path is the lower amount of violence that one does to the crystal by the techniques that are involved -- putting down either alloy junctions or Schottky barriers. The progression that we have been following was diffusing in the grating, which goes on, of course, at the standard diffusion temperature, but then dropping down to the alloying temperature in the case of aluminum-silicon at 500°C. Finally with Schottky barriers, as you say, one could think of putting down the grating patterns on polycrystalline material and on thin films, ultimately with the hope that the grain boundary diffusion may not occur when you are doing things at these low temperatures such as putting down metals on these surfaces. So I think it does make good sense to be doing that.
- Q: Did you propose that the space in between the grids be two depletion widths, whereas Professor Loferski suggested that it be two diffusion lengths?
- A: Yes. I pointed out that the advantage of two depletion layer widths is that you completely deplete the surface there, so it is a high-field region and any electron holes generated in that space-charge region are more readily collected. If, instead, you have two diffusion lengths, then the surface effects and recombination will be important since the carrier has to diffuse toward the metal grid.
- C: This cell has a depletion layer in it and the ones I am talking about don't. Ours is just a uniform layer of lines and then we have them less than two diffusion lengths apart. In this case you are putting this depletion layer on top.
- A: Yes. About a year ago, one of my graduate students had a short project of making a solar cell using the grating not at two depletion widths, but maybe 300 microns apart, and he measured an efficiency of eight to ten percent. This has now been done for the coarse grid, and we have made some devices with areas one-half centimeter squared.
- Q: May I also ask how you computed the theoretical efficiency in terms of the thermal generation current? Was that based on silicon alone, or was it also based on thermionic emission over ---?
- A: I first calculated the efficiency in the depletion width, which I think contributes about 80 percent of the total current and then there is about 18 percent from one diffusion length of the substrate and maybe less than two percent from the thermionic emission.
- Q: Is that for one wavelength?
- A: No, it is over all wavelengths -- the integral from the 0.4 micron to 1.1 micron.
- Q: Doesn't 80 percent sound pretty high for one micron?
- A: 8 percent.
- Q: 8 percent or 80?
- A: 8 percent.
- C: Yes, but you are dealing with short-circuit current if I understand you correctly. I am focusing attention on the open-circuit voltage.
- A: The open-circuit voltage depends on the temperature in the cell; at 450°K, I think it is around 0.30 or so. So the open-circuit voltage varies from 0.30 to 0.45, say, from room temperature up.



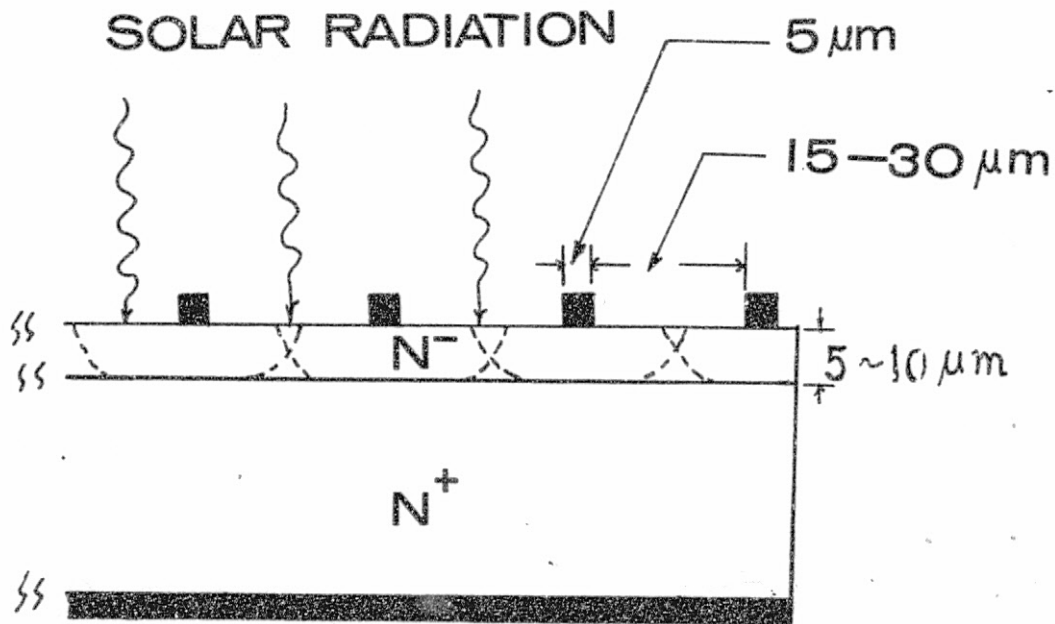


Fig. 1. Enlarged portion of the active area of a grating-type silicon Schottky-barrier solar cell. Complete structure is shown in Fig. 2. Dashed line shows that extension of depletion region over N<sup>-</sup> layer.

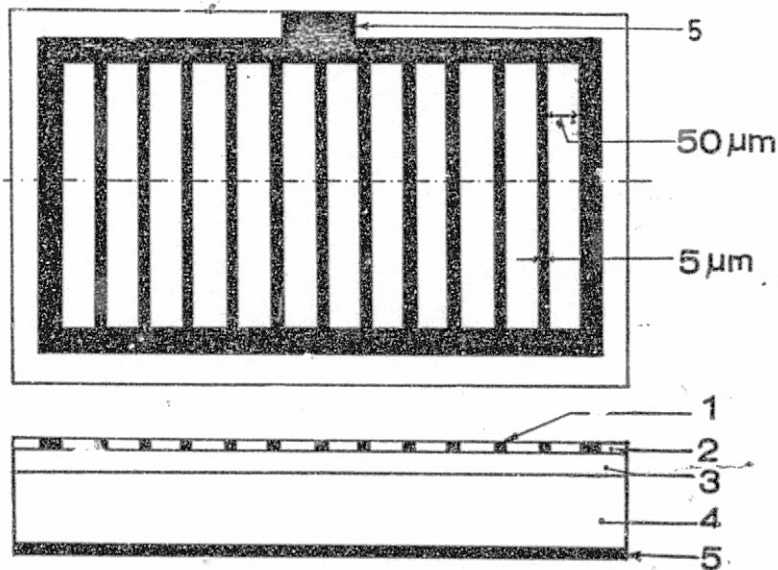
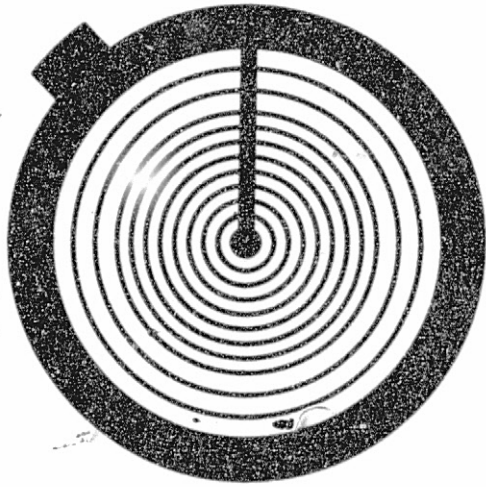
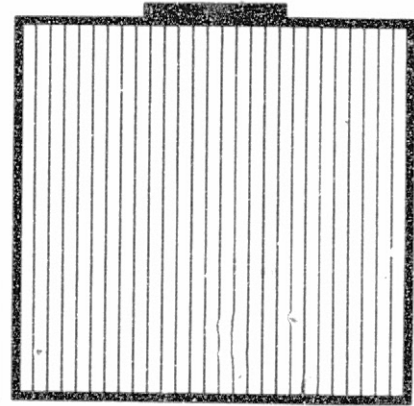


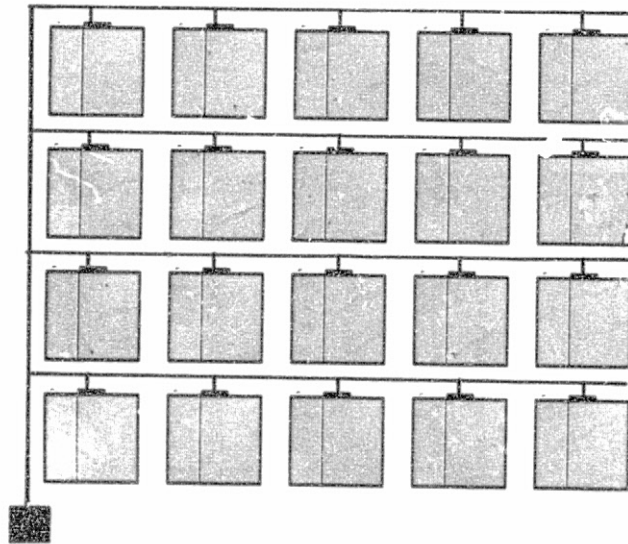
Fig. 2. A typical design of a grating-type silicon Schottky-barrier photovoltaic cell with rectangular geometry: (1) metal grids; (2) SiO<sub>2</sub> (~1000 Å) or SiO (~800 Å); (3) high resistivity silicon layer (~10 μm); (4) low resistivity silicon substrate (5 - 10 mils); (5) ohmic contact



(a)



(b)



(c)

Fig. 3. Top view of the proposed grating-type silicon Schottky-barrier photovoltaic solar cell:  
(a) circular cell, (b) rectangular cell, (c) integrated solar array in parallel

## LOW COST GaAs LAYERS ON OXIDE SUBSTRATES FOR SOLAR CELL APPLICATIONS

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### Presentation Summary

The most efficient solar cells to date have been manufactured from GaAs. However, the cost of GaAs single crystals has cast doubt on the use of GaAs solar cells as a means for competitive conversion of solar energy. The advantages for the use of GaAs over other semiconductor materials for solar cells (Ref. 1) are that: (1) its energy bandgap coincides with the solar energy spectrum for the most efficient photovoltaic energy conversion; (2) only a 1  $\mu\text{m}$  thickness is required for almost complete absorption of the sunlight; (3) it allows junctions operable to 300°C; and (4) its performance is less affected by electron and proton irradiation.

The cost of GaAs solar cells could be significantly reduced if 5  $\mu\text{m}$  thick epitaxial layers of GaAs were available on inexpensive substrate materials, such as ceramics or fused quartz. Presently, these cells are constructed on GaAs single crystals 500  $\mu\text{m}$  thick that cost roughly \$1000/ft<sup>2</sup>, based on a minimum cost of \$4/g for single crystal boules. The raw cost of Ga and As, however, is considerably less, approximately \$0.30/g combined, hence, a 5  $\mu\text{m}$  layer of GaAs epitaxially deposited on a cheap substrate for a solar cell would approach \$1/ft<sup>2</sup>. Thin layers of GaAs in square mile proportions will not deplete the available resources for Ga and As. In addition, if thin layers were accidentally volatilized, there would be considerably less arsenic available to form toxic compounds.

The context of this paper is on the potential growth and use of liquid phase heteroepitaxial GaAs on oxide substrates. The heteroepitaxial growth of several III-V compounds, including GaAs, on Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> and BeO has been done by several vapor phase epitaxial methods (VPE)-(Refs. 2,3). In addition, GaN has been grown on Al<sub>2</sub>O<sub>3</sub> by the liquid phase epitaxial method (LPE) (Ref. 4). For homoepitaxial growth of GaAs there are several advantages for LPE over VPE: (1) the raw materials costs and material losses are lower; (2) the electrical quality of the layer is enhanced by the low distribution coefficients of impurities at the interface between liquid Ga and the solid GaAs; (3) the liquid-solid interface attachment and nucleation density can be controlled with the use of a temperature gradient normal to the interface; (5) faster growth rates can be obtained; (6) Ge can be used as a p-type dopant (Ref. 5); (7) diffusion and autodoping can be employed during growth; and (8) uniform growths can be obtained on any substrate orientation. In addition, mass production of epitaxial GaAs by LPE is also possible.

The advantages for LPE homoepitaxial growth should also stand for heteroepitaxial growth. To demonstrate this possibility, our LPE GaAs homoepitaxial growth studies have shown that nucleation and growth on all substrate orientations proceeds on (100) planes in [100] directions (Figs. 1-4). The (100) planes, however, grow into (111) planes to minimize the liquid-solid interfacial energy. Similar growth morphologies are also observed for homoepitaxial GaAs VPE growths. Dependent on substrate orientation, growth normal to the substrate can become very unstable unless the liquid-solid interface is localized with respect to thermal fluctuations (Fig. 5). For heteroepitaxial VPE growths of GaAs on Al<sub>2</sub>O<sub>3</sub> the (111) GaAs orientation is obtained almost independent of the substrate orientation. In addition the layers are made up of triangular hillocks or triangular grains that vary in orientation from a few tenths to several degrees. As the triangular hillocks become smaller, more uniform layers are obtained - but only under very controlled growth conditions. Similar growths are observed in heteroepitaxial LPE on the sides of graphite and quartz crucibles, on the surface of the Ga melt, and on oxidized GaAs substrates. The latter commonly occurs for growth temperatures below 600°C, where the Ga<sub>2</sub>O<sub>3</sub> on the substrate is not reduced by the hydrogen ambient. Growth on oxidized surfaces of GaAs can be controlled if a steep temperature gradient is imposed normal to the liquid-solid interface.

Therefore, with the control of the liquid-solid interface growth conditions, heteroepitaxial LPE growths should be explored as a means to grow high quality GaAs layers on oxide substrates. The actual orientation of the substrate and its crystallinity may not be significant, since bonding may be of the van der Waals type rather than ionic and/or covalent.

A technique has been developed to control the liquid-solid interface using the temperature gradient cell shown in Figs. 6 and 7 (Ref. 6). A very stable gradient is induced normal to the substrate by flowing He through the fused quartz heat transfer tube. The Ga reservoir underneath the growth cell improves the heat transfer and flattens the temperature profile over the plane of the substrate. Uniform homoepitaxial layers from 0.2  $\mu\text{m}$  to 30  $\mu\text{m}$  thick have been grown with 300°K/77°K free carrier mobilities as great as 8600/100,000  $\text{cm}^2/\text{v-sec}$  in the low  $10^{14} \text{ cm}^{-3}$  range.

There are several distinct physical advantages gained by epitaxial GaAs solar cell layers grown on a dissimilar substrate material. For a substrate transparent to solar radiation, the p-n junction in the layer would be totally exposed to the sunlight and the active layer would be protected from environmental degradation. Interdigital electrodes would be placed on the back surface of the cell alternating between diffused p-n junction regions. This cell design would allow direct heat removal from dissipation in the junction and electrical contact area and maintain high efficiencies, especially for solar cells exposed to concentrated solar illumination.

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### Discussion

- Q: We have worked with gallium arsenide thin films using chemical vapor growth on substrates like moly or aluminum and have obtained five percent cells. One thing that is a problem about the LPE technique is how to handle large areas. It seems that for terrestrial purposes, area is the main consideration. We have to assume you are going to be able to get high efficiencies over ten percent, but I don't see how you are going to use this technique. Can you analyze what the area problems would be in LPE?
- A: We are not manufacturers of materials; however, we do feel that some of the techniques that we have developed in handling substrates and the consequent growths are useful. We can envision mass production types of facilities which are essentially self-cleaning – you pull out a substrate, for instance, a long ribbon or sapphire from a spool and through a gallium melt, with a layer grown on it in a continuous manner, basically using a steady-state type of transport during the liquid phase epitaxial growth. I am not prepared to say that we can grow a foot at a time, but we can grow several square inches at a time.
- Q: You mentioned a possible cost of your five-micron epi-layer in the range of \$1.00 a square foot. Will you comment on the cost of the sapphire or spinel that you will need?
- A: I didn't mention that we are essentially proposing to do the work on some of these more expensive substrates—principally sapphire and spinel—because we can perhaps understand better the attachment kinetics or growth on these substrates. We hope eventually to show that growths can be achieved from fused quartz, for instance, or other types of cheaper materials, as well as on sapphire and other materials which can be grown in ribbon form. I haven't really figured substrate costs into a one dollar per square foot.

- Q: What kind of efficiencies do you project that we could get out of these cells? Have you thought about that at all? Are these going to be similar to the cells that IBM made? Or is this a materials program?
- A: This is principally a material program. However, some of the results that IBM has published using gallium-aluminum heterojunction, can be achieved, for instance, on sapphire by essentially auto-doping from the substrate into the layer. Surface recombination at the oxide semiconductor interface may be a very severe limitation; these are problems we would like to explore. It may appear that some of the attachment is more of a Van der Waals type of bonding to the substrate rather than ionic or covalent. Lowered surface state densities may be achieved by doing growths at lower temperatures.

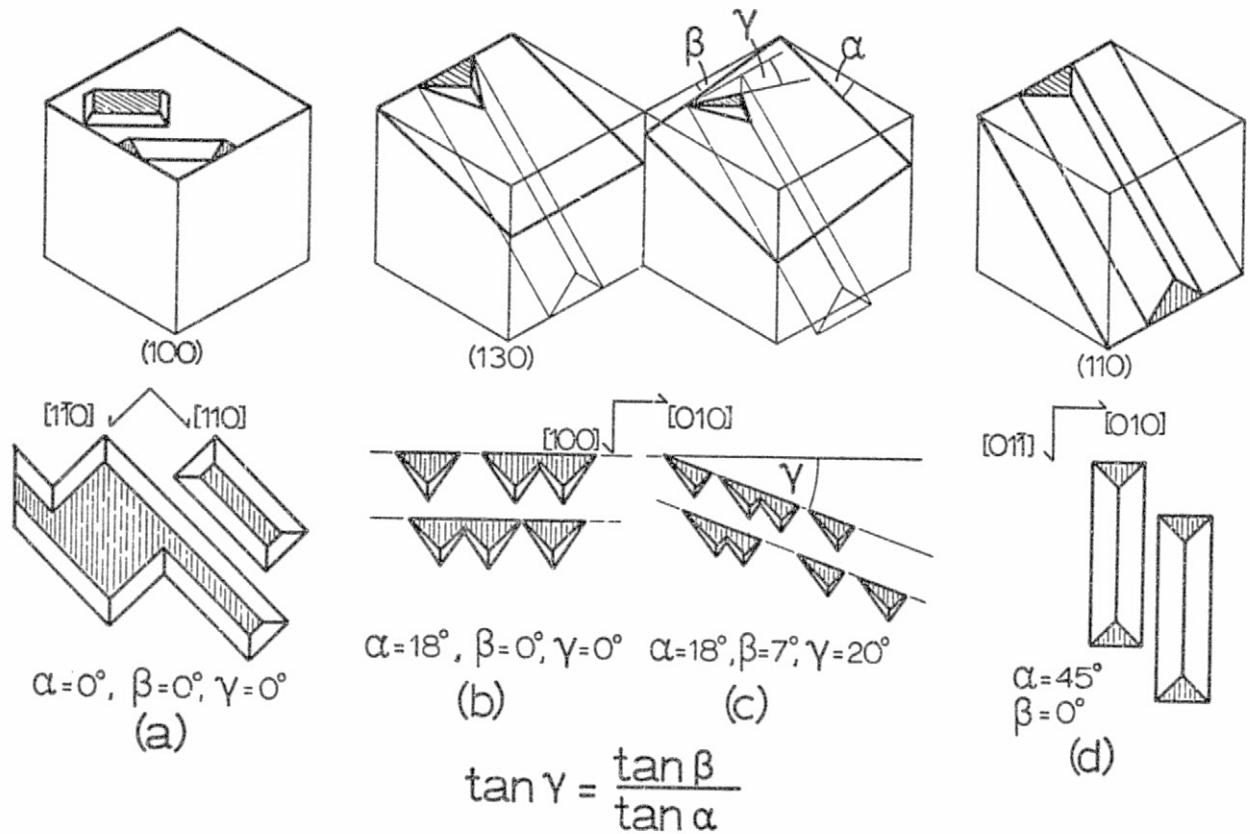


Fig. 1. Schematic orientation relationships between nucleation hillocks and substrates rotated about a  $[100]$  axis. The shaded and unshaded hillock surfaces are  $(100)$  and  $(111)$  planes, respectively. The orientations of surface terraces parallel these hillocks as illustrated in (b). For slight misorientations, as illustrated by (c), the terraces will change direction by an angle  $\gamma$ , given by  $\tan \gamma = \tan \beta / \tan \alpha$ .

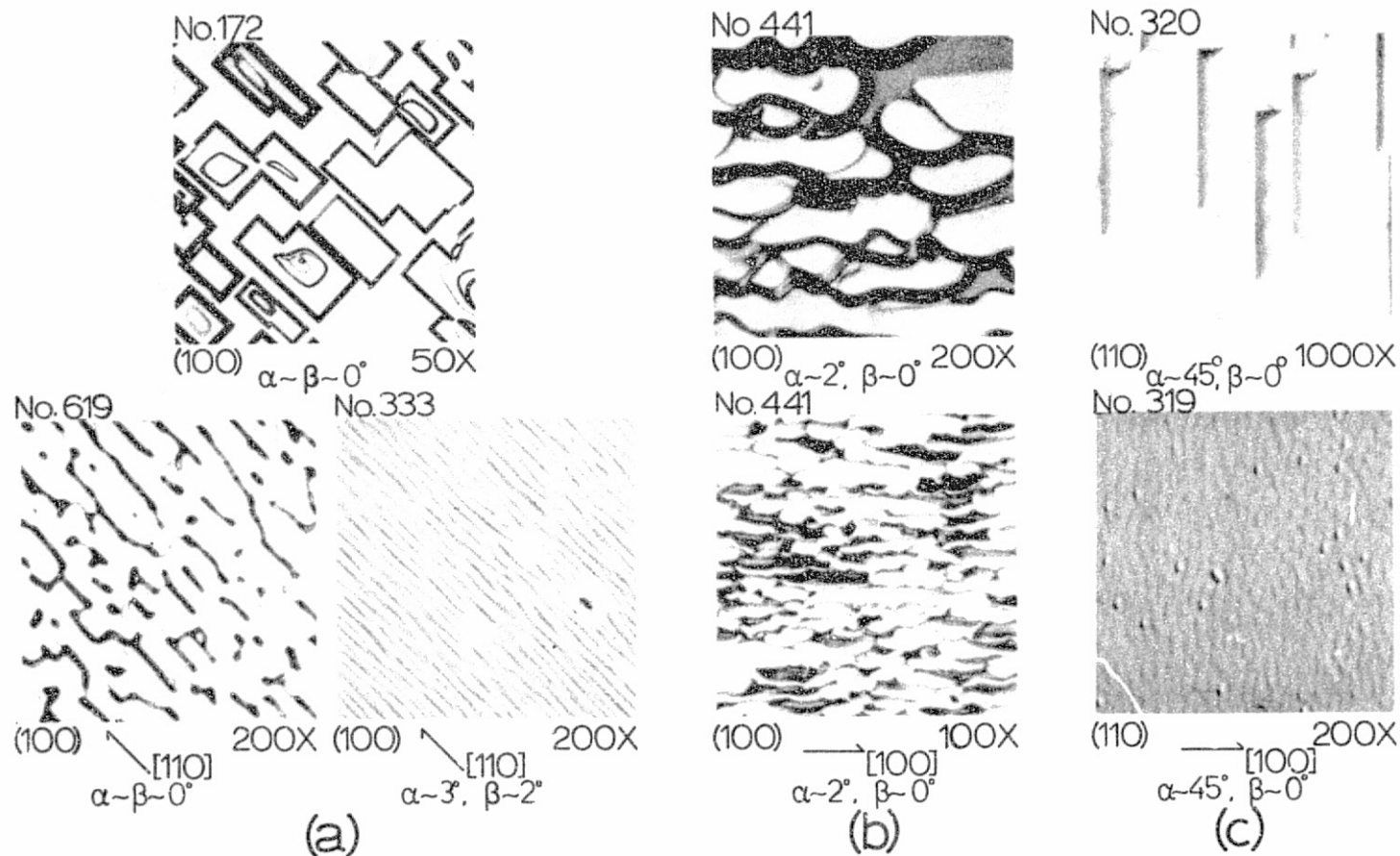


Fig. 2. Characteristic nucleation hillocks and surface terraces observed on (100) substrates, (a) and (b), and (110) substrates, (c). The hillocks and terraces are principally bounded by (100) and (111) planes. The angles correspond to the schematic orientations of the substrates shown in Fig. 1. The terrace orientations shown are for a (100) plane rotated (a) slightly about a [110] axis, (b) slightly about a [100] axis and (c)  $45^\circ$  about a [100] axis.

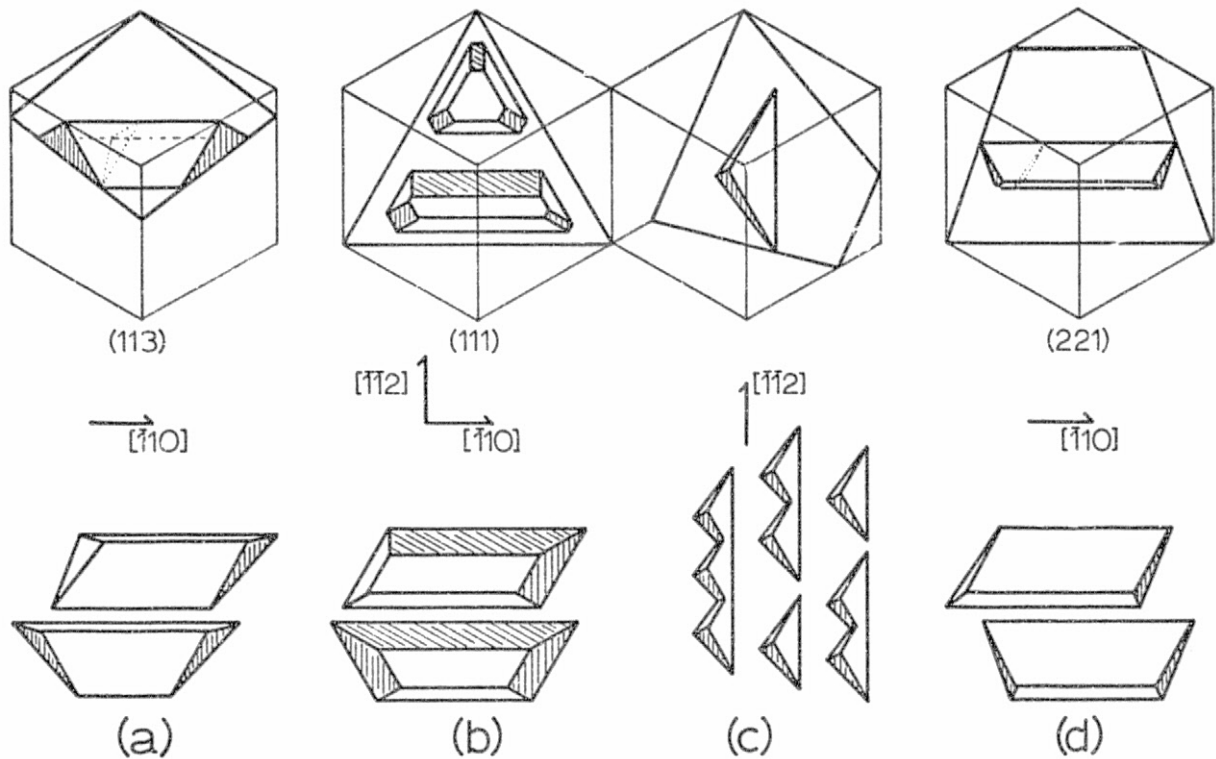


Fig. 3. Schematic orientation relationships between nucleation hillocks and substrates rotated about a  $[100]$  axis. The shaded and unshaded hillock surfaces are  $(100)$  and  $(111)$  planes, respectively. The nucleation hillocks in (a), (b) and (d) parallel the  $(100)$  and the  $(110)$  prismatic hillocks. For a rotation about a  $[\bar{1}\bar{1}2]$  axis, (c), the nucleation hillocks coalesce together into extended platelets along that axis.



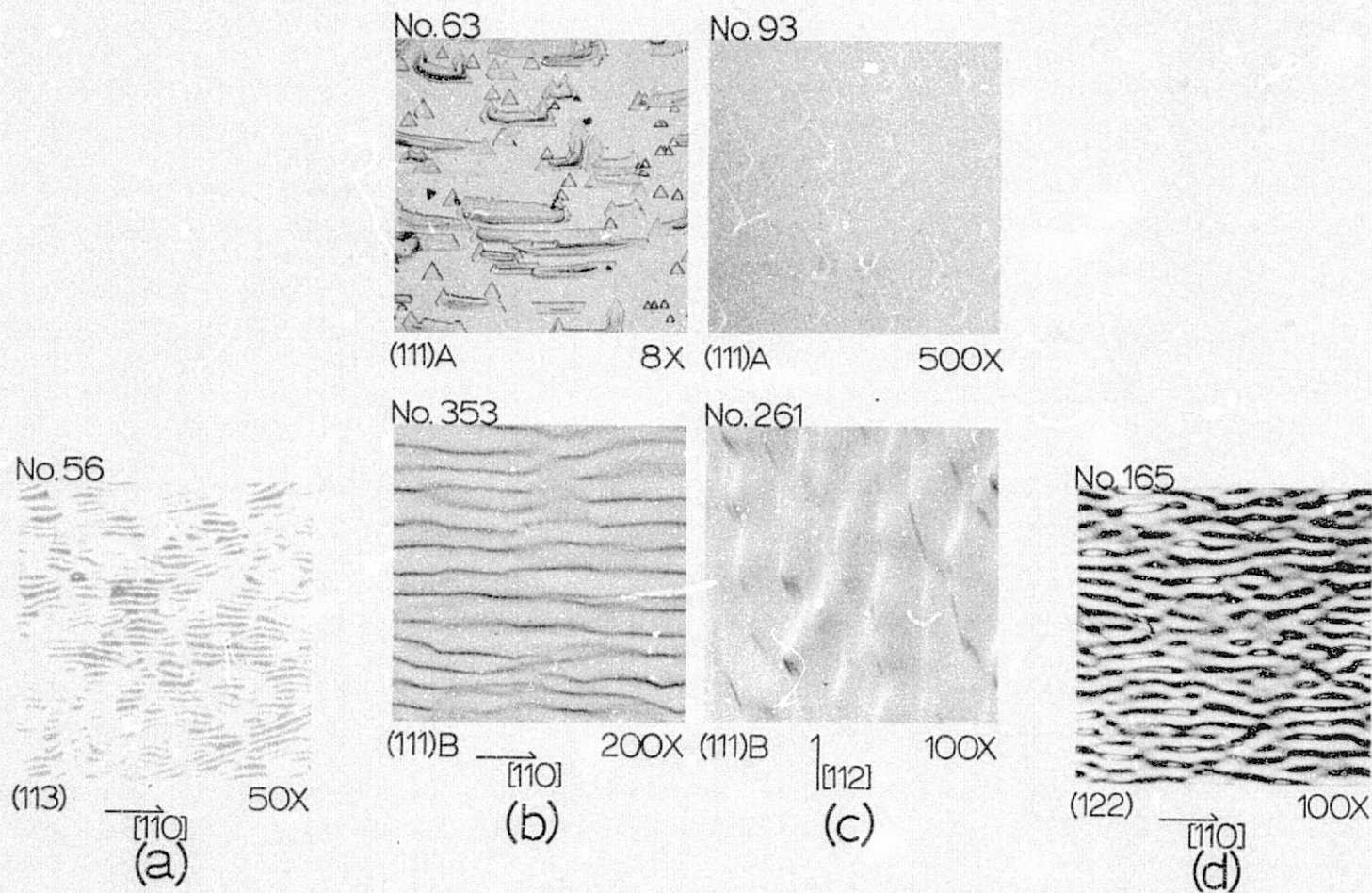


Fig. 4. Characteristic nucleation hillocks and surface terraces observed on (a) (113), (b) and (c) (111), and (d) (122) oriented substrates. The hillocks and terraces are principally bounded by (100) and (111) planes. The hillocks and terraces correspond to the schematic orientations of the substrates shown in Fig. 3. The terrace orientations shown are for a (111) plane rotated (a) about a [110] axis to a (113) plane, (b) slightly about a [110] axis, (c) slightly about a [112] axis and (d) about a [110] axis to a (122) plane.

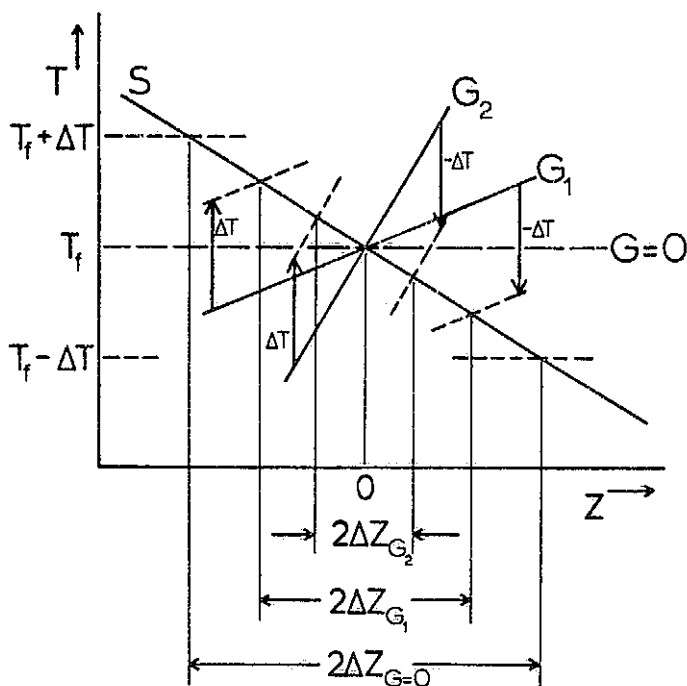


Fig. 5. The effect of thermal fluctuations,  $\pm \Delta T$ , and temperature gradient,  $G$ , on the position of the liquid-solid interface along the curve  $S$ , for an interface temperature  $T_f$ .

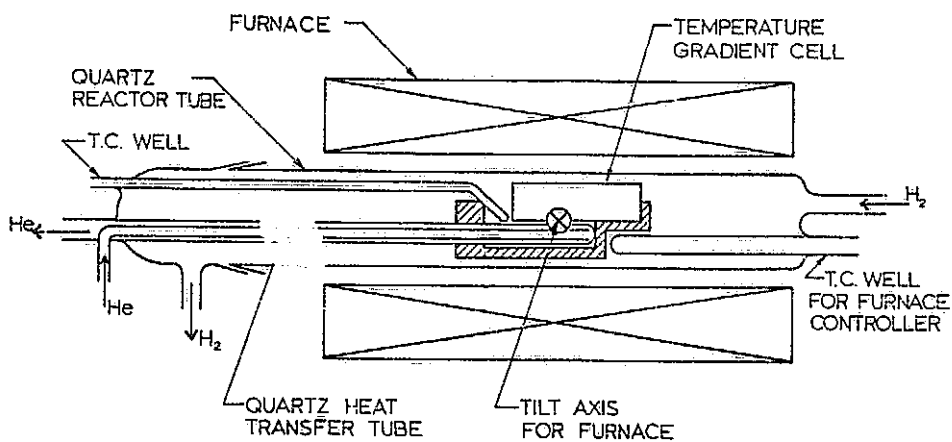


Fig. 6. Horizontal Tilt System with Temperature Gradient Cell in Place

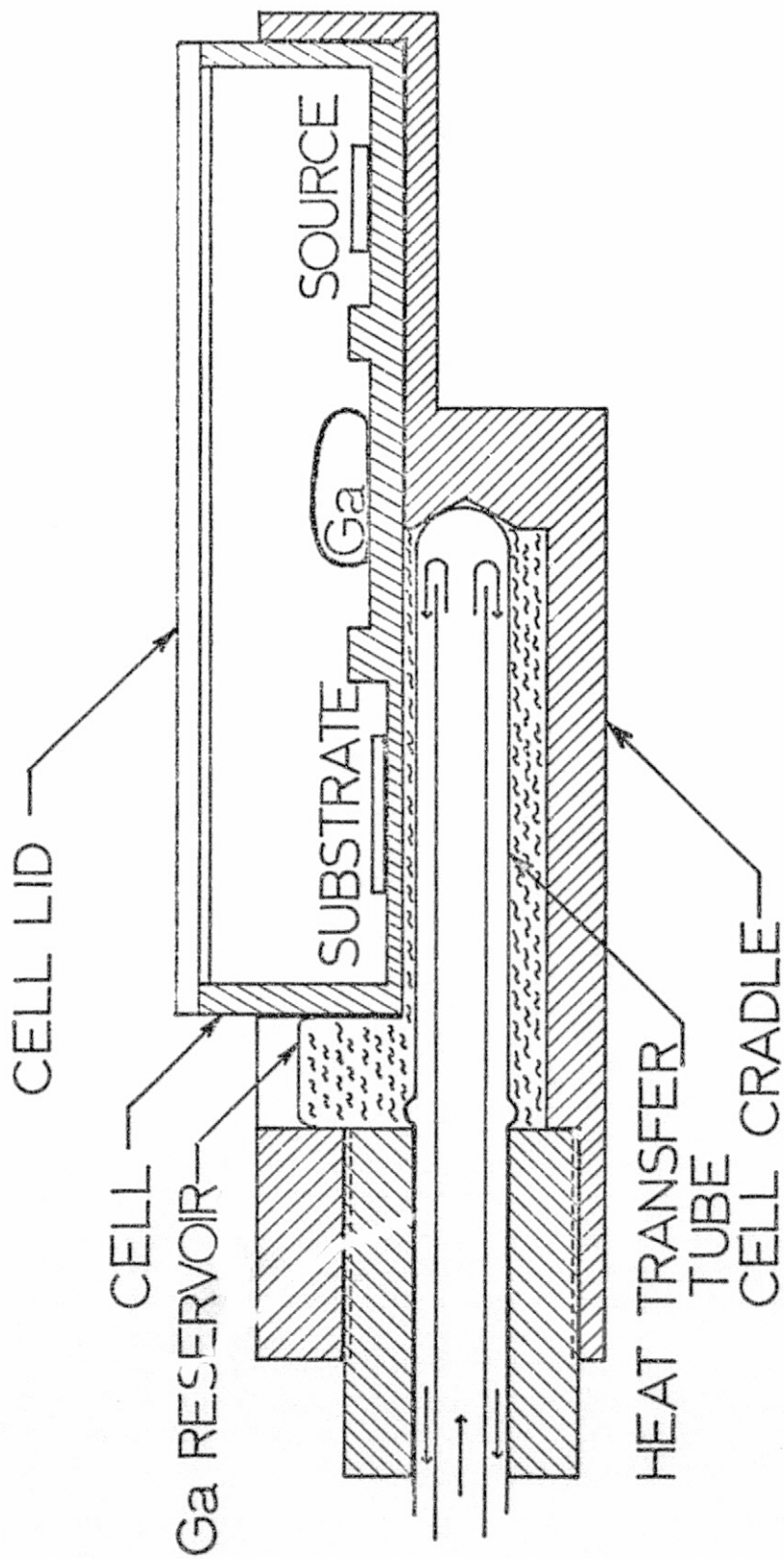


Fig. 7. Details of the Temperature Gradient Cell

## GROWTH OF GaAs SINGLE CRYSTALS IN RIBBON FORM

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### Presentation Summary

#### Introduction

The potential of gallium arsenide for photovoltaic energy conversion has been recognized for many years. Gallium arsenide is a direct-gap semiconductor. It can, therefore, operate effectively at a thickness of a few microns compared to at least 100 microns for silicon, thus permitting a substantially lower weight. Furthermore, the bandgap of 1.42 eV for GaAs is close to the theoretically optimum for solar energy conversion. Gallium arsenide can be heated to higher temperatures than silicon without loss in conversion efficiency, and is also more radiation resistant.

#### General Approach

The basic concept is shown in Fig. 1. A thin ribbon of GaAs is supported upon a woven high-purity quartz or graphite belt which is impregnated with boron oxide ( $B_2O_3$ ) glass. The semiconductor ribbon is protected (encapsulated) by the upper belt, which is also impregnated with  $B_2O_3$ . The upper and lower belts are maintained at a temperature above  $450^\circ C$  (which is the softening/flow temperature of boron oxide), thus the belts retain a continuous flexible molten glass interface with the semiconductor material. Note that the boron oxide is relatively inert to the III-V compound semiconductors so that the process is not restricted to GaAs production and may be considered a generic process for a wide variety of the compound semiconductors.

The method of operation is shown in Fig. 2. A thin ribbon of polycrystalline feed material in appropriate stoichiometry (in the form of preferably somewhat densified fine powder aggregate, vapor-deposited film, etc.) is fed onto the lower heated quartz belt, which is impregnated with a continuous molten layer of  $B_2O_3$ . The upper tape then joins the lower, sealing the upper surface of the feed material as shown in Fig. 3. Before the recrystallization step, the system must be free of oxygen and a protective atmosphere must be provided. The heat source (RF induction coupling, radiational, dielectric or other) produces a narrow molten zone across the polycrystalline ribbon adjacent to a suitable single-crystal seed. The tapes, impregnated with molten  $B_2O_3$ , prevent decomposition of the volatile compound. Downstream of the molten zone, the recrystallized region remains sealed by the upper and lower tapes until the temperature of the GaAs is sufficiently low to permit exposure to the ambient inert atmosphere without decomposition – but still above the melting point of the boron oxide on the tape. The tapes are then separated from the crystal ribbon and the GaAs ribbon is washed in hot water to remove the residual boron oxide.

Several methods of heating are possible. Direct RF induction coupling to the compound semiconductor (7-10 MHz) could be used with the upper and lower tapes as shown in Figs. 2 and 3. Alternatively, it may well be possible to eliminate the upper tape entirely and provide merely a thicker layer of transparent molten  $B_2O_3$  atop the feed material. Thus it would be possible to consider the use of a radiant heat source (strip heater, xenon lamp, laser, etc.) from above, which would transmit through the transparent upper  $B_2O_3$  layer and melt the encapsulated GaAs.

The simplest method of feed preparation would be to doctor powdered aggregate onto the supporting tape as shown in Fig. 2. The feed ribbon could also be deposited by thin film forming methods (sputtering, vapor deposition, etc.) onto the fluid  $B_2O_3$  layer on the surface of the lower tape.

The vapor pressure of the volatile constituent of the molten compound must be balanced by the ambient pressure surrounding the upper and lower support tapes. Two or three atmospheres of nitrogen would be sufficient for GaAs growth (assuming that the  $B_2O_3$  film is continuous).

### Laboratory Feasibility Demonstration

#### a. Theoretical Analysis

The program will be initiated with a detailed theoretical analysis of the stability of the ribbon-like molten GaAs in contact with the liquid boron trioxide encapsulant. Coupled with this analysis will be a detailed study of the heat transfer between various heat sources (resistance, RF induction, and laser) and the feed material/molten zone as well as control of thermal gradient and thermal losses. While static conditions can be readily analyzed, attempts will be made to predict dynamic behavior of the ribbon-growing operation. This task will be based upon the methods used for the analysis of the floating-zone oxide fiber drawing process developed at our laboratories as well as the extensive background in liquid-encapsulated crystal production available at Arthur D. Little, Inc. Preliminary calculations have shown that the width of the molten zone should be about 10-15  $\mu$  for 5- $\mu$ -thick GaAs. The zone may be arbitrarily long.

#### b. Design and Construction of the Feasibility Model

Based upon the analytical data which is developed as well as the extensive background in the design and construction of sophisticated crystal-growing furnace systems, we shall initiate the design of a simple furnace unit to demonstrate the feasibility of producing GaAs substrate in ribbon form. The goal of this initial phase of the work shall be the preparation of GaAs single-crystal ribbon having typical dimensions of 10-cm length, 1-cm width, and minimum thickness. It will be necessary to design the apparatus so that various heating methods may be investigated and the molten zone readily monitored and controlled.

We do not plan to produce the substrate ribbon continuously during this phase of the program; however, it is anticipated that the model will provide the basis for the design of a continuous ribbon production system.

#### c. Experimental Operation of the System

Testing will include an evaluation of various heating methods (resistance, RF induction, and possibly laser sources), physical properties of the feed material (particle size, distribution, and method of support), and stability of the molten encapsulant, i.e., compatibility with various support structures and retention of the GaAs ribbon.

Attempts will be made to propagate and move a uniform narrow molten zone through the feed material to produce a recrystallized GaAs strip.

Since the furnace unit must operate under an inert atmosphere, the chamber will be leak-checked under vacuum and positive pressure conditions while at room temperature and at operating temperature to insure the integrity of the system.

Following the operation of the basic apparatus, we shall carry out any modifications necessary to optimize operation. Rapid response to our requirement is insured by the close interchange established with our model shop.

#### d. Production of Samples

Upon completion of the evaluation and modification of the furnace unit as well as integration of the selected heating source, we shall proceed with a series of experiments to evaluate the stability of the GaAs molten zone. The experimental program will be based upon the theoretical analysis and conclusions drawn in Task a. Our initial experiments will be concerned primarily with the propagation and movement of the thin molten zone through the feed material aggregate in an effort to produce a solid ribbon of polycrystalline GaAs. Once the parameters for continuous zone stability have been established, we shall attempt to seed the molten zone to produce single-crystal ribbon.

SESSION V. OTHER MATERIALS AND DEVICES -- BERKOWITZ

The goal of Phase I of this program will be the preparation of 10 cm long by 1 cm wide single-crystal GaAs ribbon of minimum thickness.

**Discussion**

(Not recorded)

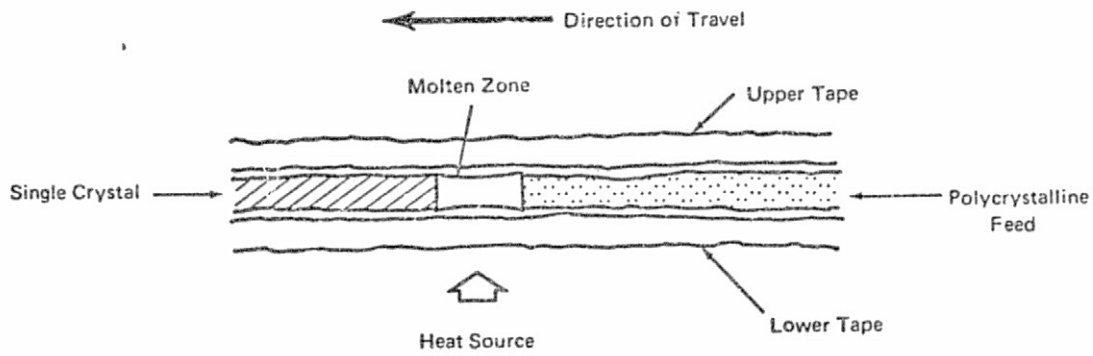


Fig. 1. Basic Concept

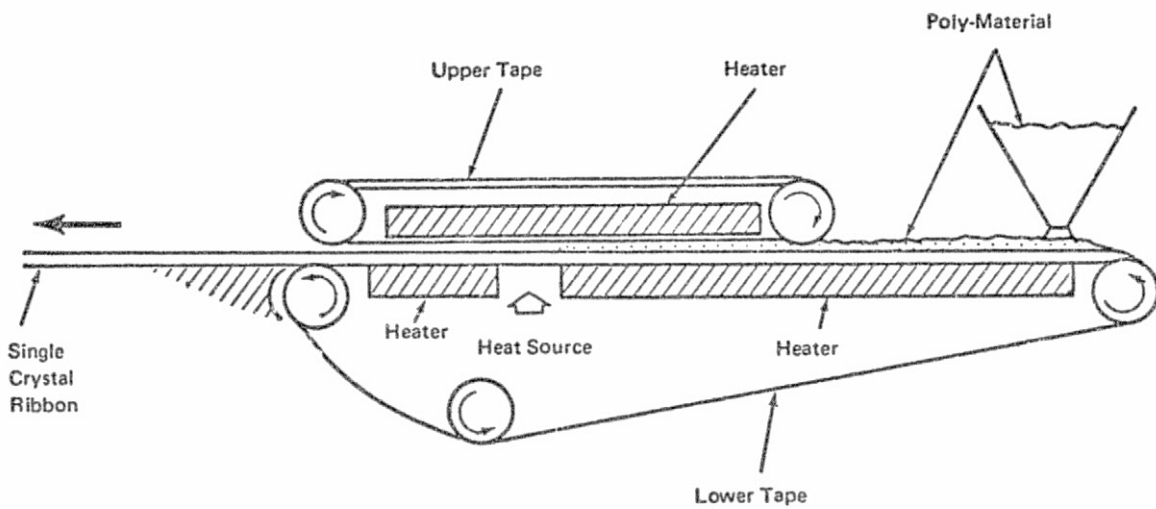


Fig. 2. Method of Operation

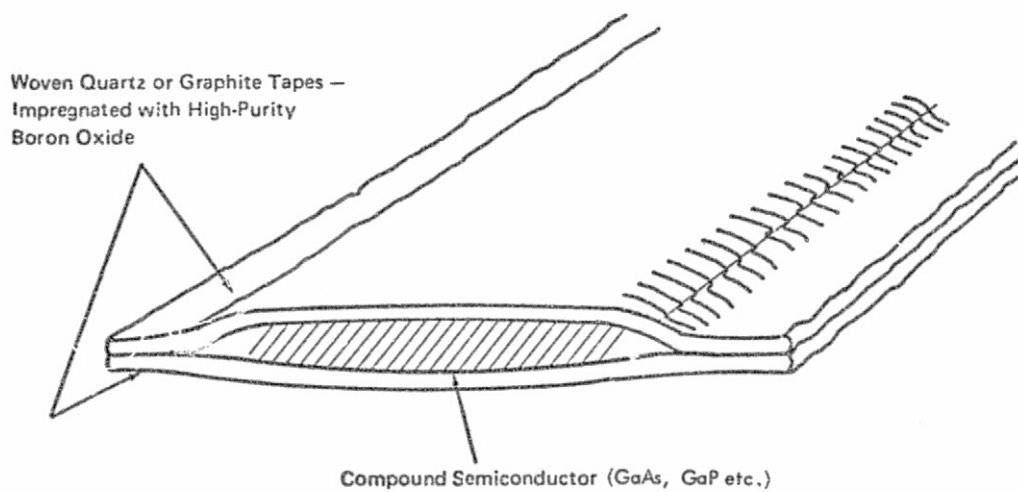


Fig. 3. Cross-Section Gallium Arsenide Ribbon Production

STATUS AND PROJECTIONS FOR Ga<sub>1-x</sub>Al<sub>x</sub>As-GaAs SOLAR CELLS

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**Presentation Summary**

The main problems affecting GaAs solar cells have been largely solved by using a Ga<sub>1-x</sub>Al<sub>x</sub>As layer as thin as possible grown onto the surface of a GaAs p-n junction solar cell (Refs. 1, 2, and 3). Surface recombination, shunt resistance, and series resistance problems are greatly reduced by this layer, which acts as a transparent ohmic contact while greatly reducing the surface state density on the GaAs surface. The AMO efficiency of the best of these devices to date is 12%, 12.8% after correction for contact area, for a Ga<sub>1-x</sub>Al<sub>x</sub>As thickness of 3 microns. Typically,  $V_{oc}$ 's are 0.94 to 1.0 volt,  $I_{sc}$ 's are 20 to 23 mA/cm<sup>2</sup>, and F.F.'s are 0.78 to 0.81.

Figure 1 shows a computer-calculated projection for pGa<sub>1-x</sub>Al<sub>x</sub>As-pGaAs-nGaAs devices as a function of thickness. It has been assumed that the recombination velocity at the surface is high, 10<sup>6</sup> cm/sec, and 10<sup>4</sup> cm/sec at the interface. The AMO efficiency can easily exceed 17% for 1- $\mu$  thicknesses and 20% for 1000 Å or less, in spite of the high recombination velocity at the surface. Work toward obtaining devices with these thicknesses is going on, and it is not expected to be difficult to obtain units with submicron layers. AMO efficiencies of 15% or over seem feasible within 1 to 2 years for a development cost of around \$100,000, based on the existence of nearly 13% cells now with clear understanding of the inner workings of the device.

Calculations similar to Fig. 1 for AM1 and AM2 predict efficiencies of 22 and 24%, respectively, under the same conditions (1000-Å layer). Values of 16% and 20% have been measured at AM1 and AM2, respectively.

The ultimate cost of these devices is likely to remain high, limiting their usefulness to satellite and other special applications. The cost is largely determined by the scarcity of Ga, since the liquid phase epitaxy and diffusion processes involved are not much more complicated from a production basis than processes for producing Si devices. New sources of Ga or higher estimates of its relative abundance would be necessary to impact this outlook. On the other hand, GaAs solar cells require active regions only about 5 microns in thickness, and some sort of mating of thin film cells with the principles of the Ga<sub>1-x</sub>Al<sub>x</sub>As-GaAs devices could lead to lower costs and lower efficiencies, but much improved efficiency/cost ratios.

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**Discussion**

(Not recorded)



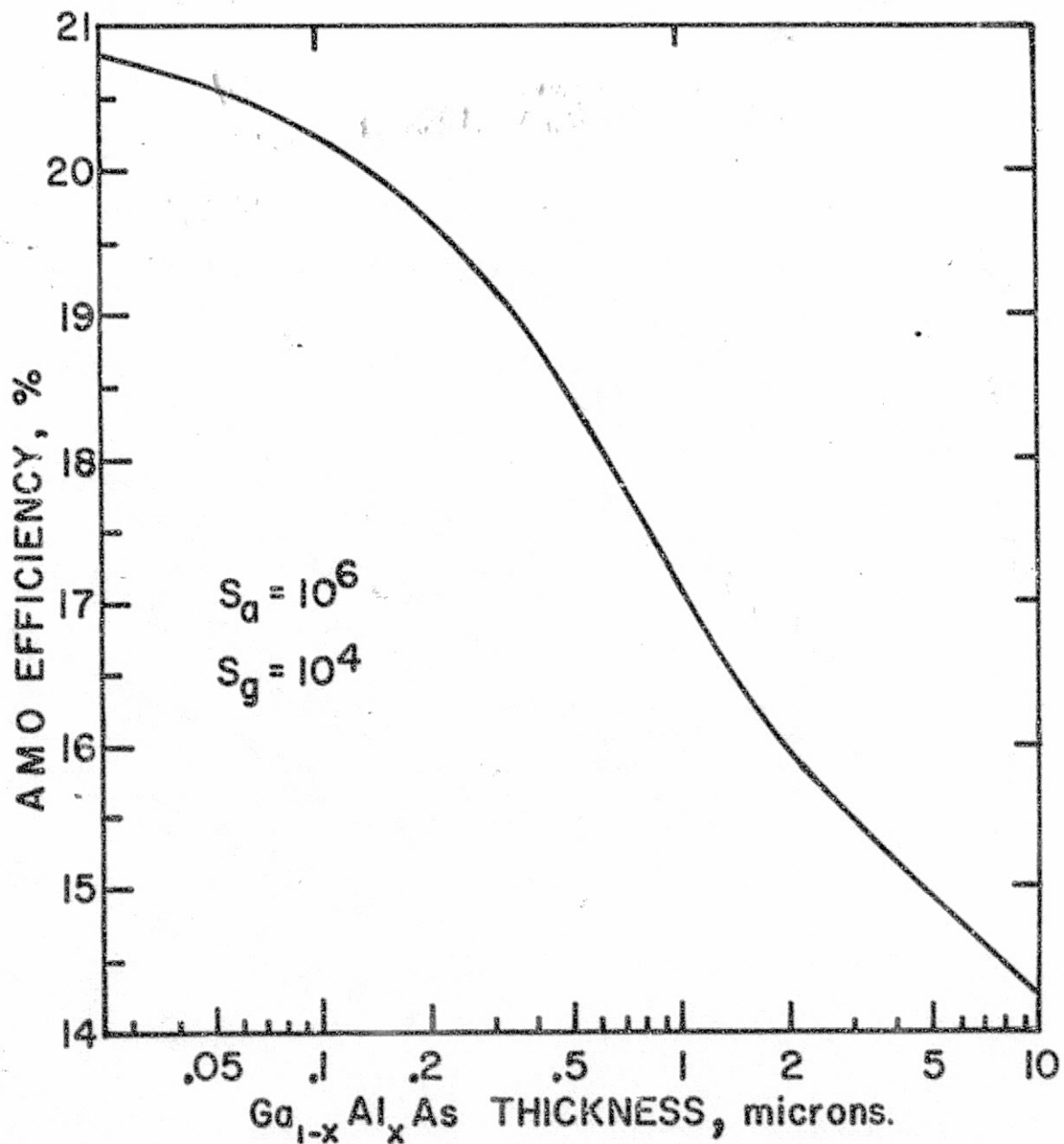


Fig. 1. Calculated AMO Efficiency of  $\text{pGa}_{1-x}\text{Al}_x\text{As-pGaAs-nGaAs}$  Solar Cells As A Function of the Alloy Layer Thickness

## ORGANIC PHOTOVOLTAIC CONVERSION

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## Presentation Summary

The highest conversion efficiency attained so far with an organic system is  $\sim 10^{-6}$  (10<sup>-4</sup>%). The system consists of a thin layer of tetracene sandwiched between the metals Al and Au (Refs. 1 and 2). Table I summarizes pertinent data. With the present efficiencies significant power output can be attained by using larger area sensors. Figure 1 shows the spectral region of response. Table II summarizes typical photocarrier generation quantum efficiencies for organic materials (Refs. 3-7). This is a fundamental limitation on the solar energy conversion efficiency and indicates the upper limit for conversion efficiency. An efficiency limitation of 2 to 7% is indicated for tetracene, for example, to be compared with the currently available efficiency of 10<sup>-4</sup>%. Improved control of materials parameters can be expected to produce significant improvements in efficiency and allow a closer approach to the theoretical value. Polymer films are indicated for practical devices in view of their better film-forming capabilities. Data on PVK-TNF, an efficient polymeric photoconductor, are included indicating that similar photovoltaic conversion efficiencies should be attainable in these materials also. In the case of this material an increase in efficiency is obtained with increased field (Ref. 7). Figure 2 shows the spectral response of the PVK-TNF complex. Table III summarizes cost estimate data for currently available conversion efficiencies. With an efficiency of 10<sup>-4</sup>%, it is estimated that the cost per watt is 60-100 dollars. An efficiency improvement of 10<sup>2</sup>-10<sup>3</sup> is necessary before low cost converters (0.25 to 0.50 dollars per watt) become feasible. To summarize, such improvements could be attained by better control of carrier recombination and trapping (by control of defects and impurity levels) and the development of ohmic contacts. For practical devices, polymer systems, such as PVK-TNF, are likely to be the most useful in view of the anticipated need for large area sensors.

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## Discussion

- C: I think the 10<sup>-1</sup> percent efficiency for large scale conversion just will not do. That's a factor of 100 times the 4000 square miles of area required for power generation for the United States.
- C: The point is well taken.
- Q: What is the theoretical situation for organics? Has anybody analyzed these systems to see what the potential is for getting the efficiency up?
- A: This is what we are suggesting as to what is needed -- more work is needed in this area. We don't know to what extent this lower efficiency is due to improper control of the material, impurities, and so on, or whether it is a fundamental limitation.
- C: I think you should look at the fundamentals first before you do any experiments.
- Q: What is the bandgap in this material?
- A: The intrinsic bandgap?
- Q: Yes.
- A: PVK is estimated to be about 4.6 electron volts. That's the intrinsic bandgap.
- Q: Then, perhaps, is efficiency inherently low in principle?
- A: Yes. That's what I was just pointing out.
- Q: Are there any organic systems or polymers with bandgaps closer to the ideal one?
- A: You are talking about a mechanism of photovoltaic conversion or photovoltage production which is applicable to things like gallium arsenide and silicon. This is a different system, a different mechanism for producing photovoltages. Excited states are developed in this material, it seems. It's a different mechanism for producing photovoltage. Whether the bandgap is important or not, I don't know. I think it is important in this kind of thing.

Table I. Present State-of-the-Art Tetracene With Al-Au Electrodes

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Conversion efficiency $10^{-6}$ ( $10^{-4}\%$ )
Assuming solar intensity $1 \text{ kW} \cdot \text{m}^{-2}$ :
1 mW of energy obtained from $1 \text{ m}^2$ of area
1 W of energy obtained from $10^3 \text{ m}^2$ of area
1 kW of energy obtained from $10^6 \text{ m}^2$ of area
Disadvantage: Materials fabrication problems

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Table II. Photocarrier Generation Efficiencies for Aromatic Hydrocarbons

Extrinsic		
Tetracene	0.02-0.075	(500 nm)
Anthracene	0.01	(400 nm)
Phenanthrene	0.01-0.03	(350-250 nm)
Intrinsic		
Anthracene	$10^{-4}$	(278 nm)
Tetracene	$5 \times 10^{-3}$	(330 nm)
Pyrene	$2.3 \times 10^{-3}$	(350-250 nm)
Polymer Films		
PVK-TNF (1:1)	$2 \times 10^{-3} - 10^{-1}$	(550 nm; $10^6 - 10^8 \text{ V} \cdot \text{m}^{-1}$ )

Conclusions

- (1) Better control of materials parameters should lead to improved photovoltaic conversion efficiencies.
- (2) Large area sensors will be needed for significant power output pointing to polymer films as materials of choice in practical systems.

Table III. Estimate of Materials Cost (10<sup>-4</sup>% Conversion Efficiency)

Assuming:

Area of sensor: 1000 m<sup>2</sup> (to generate 1 W)

Organic layer thickness: 10<sup>-6</sup> m

Metal layer thickness (Al): 50 × 10<sup>-6</sup> m

Amount required (per watt):

135 kg (297 lb) of aluminum @ 20¢/lb = \$60

1 kg (2 lb) or organic @ \$1.00/lb = \$ 2

\$62

Taking a figure of \$100 per watt, an improvement in efficiency of 10<sup>3</sup> is needed to reduce the cost to 10¢ per watt.

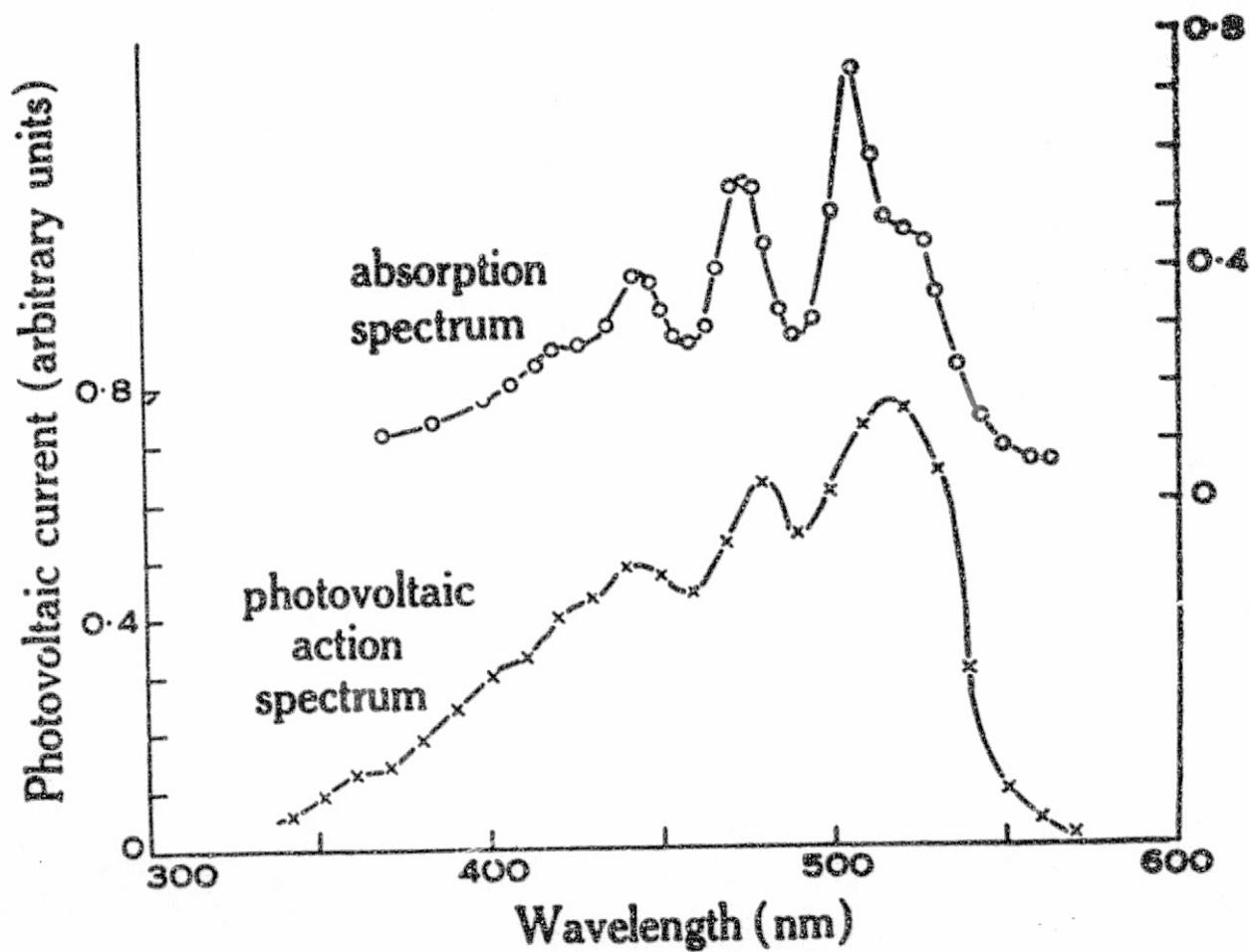


Fig. 1. Photovoltage Spectral Response and Absorption Spectrum for Al-Tetracene-Au (Ref. 1)

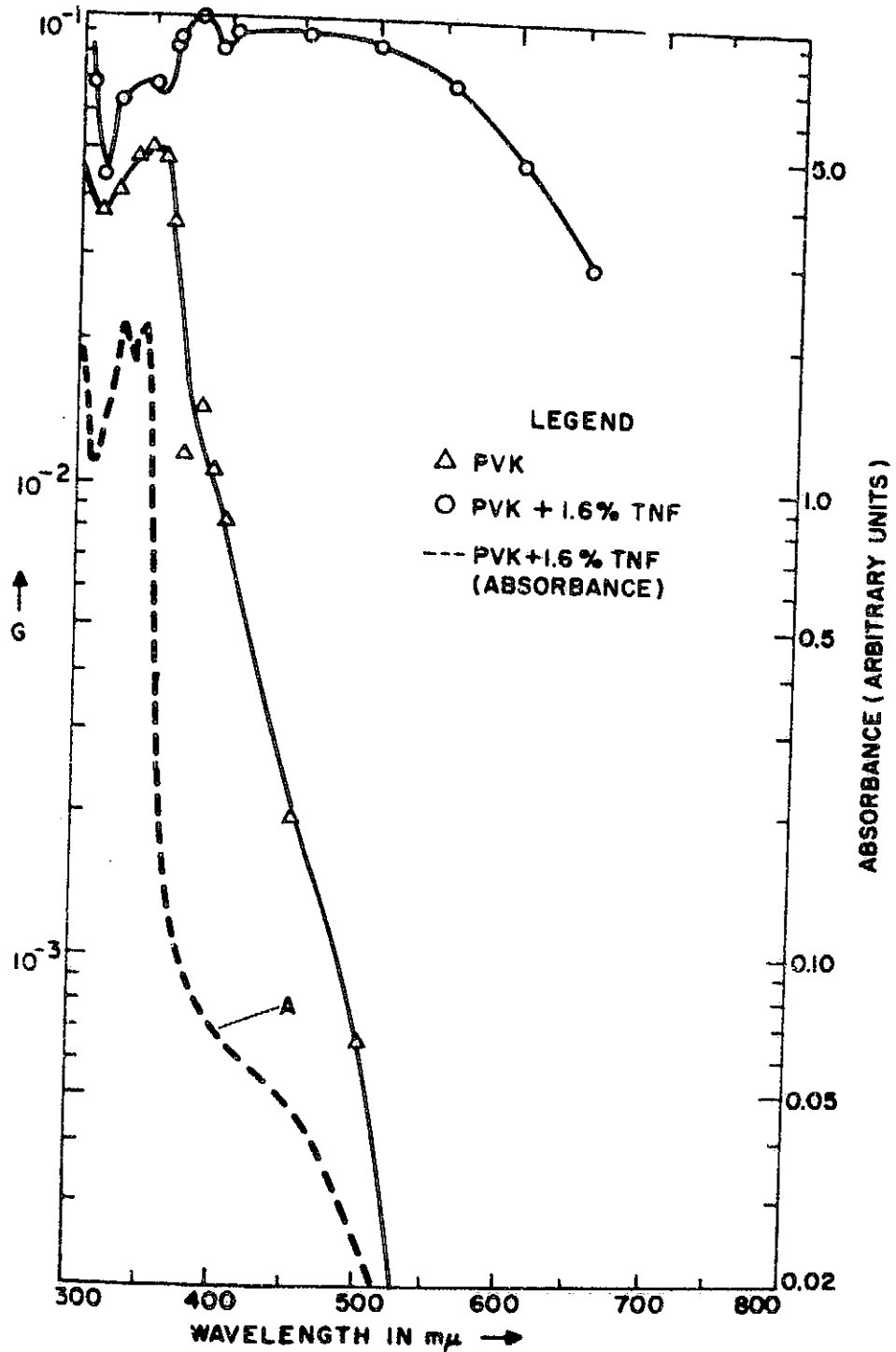


Fig. 2. Photocurrent Spectral Response and Absorption Spectrum for PVK-TNF Complex (Ref. 8)

## PHOTOGALVANIC CELLS

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### Presentation Summary

The NSF-RANN is currently supporting a research program at Boston University and Esso Research and Engineering to get economic photogalvanic cells. Photogalvanic cells are essentially batteries which can be recharged by light.

Photogalvanic cells rely on reversible endergonic photochemical reactions or reactions which can be pushed uphill with light. Current research is centered around the iron-thionine system as shown in Fig. 1. The semithionine produced by photochemical reduction of thionine by ferrous ion is electroactive. That is, it can migrate to an electrode surface and give up an electron as in Fig. 2. Simultaneously, a ferric ion is reduced at the dark electrode. The overall reaction is the reverse of the initial photochemical reaction; thus no reactants are consumed and only power is withdrawn.

Boston University is carrying out the photochemical research needed to optimize the photo yield of electroactive species, and Esso is carrying out the engineering research needed to apply the chemical systems to real cells.

### Discussion

- Q: Is the five percent efficiency based on the solar spectrum or on the absorption of a single wavelength?
- A: It's engineering efficiency. It's based on the solar spectrum. The quantum efficiency of this reaction is 1. And it's just if we could get that reactive species -- that reduced dye -- to an electrode surface; we think we can have a very highly efficient system.
- Q: Does the wavelength have to be 590 nanometers?
- A: No, it has a spread. It starts absorbing around 650 and reaches a maximum of about 590 and then drops off under 500, I believe. But with this system we have a real control here, in that we can alter the dye so that it absorbs in other areas of the spectrum. There are other dyes that do the same thing, but they absorb in different areas of the spectrum, so that by having a multidye system, we can cover different areas of the spectrum.
- Q: It's with the multidye system that you anticipate the five percent efficiency -- not for the single system?
- A: Right. Not for the single system.
- Q: What is the electrode material?
- A: The electrode material can be gold, platinum, and we have used all in the standard setup we have. There are some semiconductors that are very interesting that we are working on now that might catalyze the reaction of the leuco-thionine -- the fully reduced form of the dye -- which on normal electrode surfaces cannot give up some electrons. Or if we could find a semiconductor material that can catalyze this decomposition of the fully reduced dye, we will be in even better shape than we are now.
- Q: What is the physical separation between the electrode and the front window?
- A: For this cell here, it's about a millimeter. It doesn't absorb very much dye, or very much light. The absorption is very poor on that.

Q: So you have to have a very large — ?

A: No. You don't. If you were concentration limited, in other words if you could only have a certain concentration of dye, or if there were an optimum concentration of dye above or below which you're in trouble, then there would be a problem. But you can imagine a cell where the electrodes are parallel to the light. So, therefore, your solution could be very dilute, but you can absorb down the length of the solution and still maintain a rather close proximity to your electrodes.



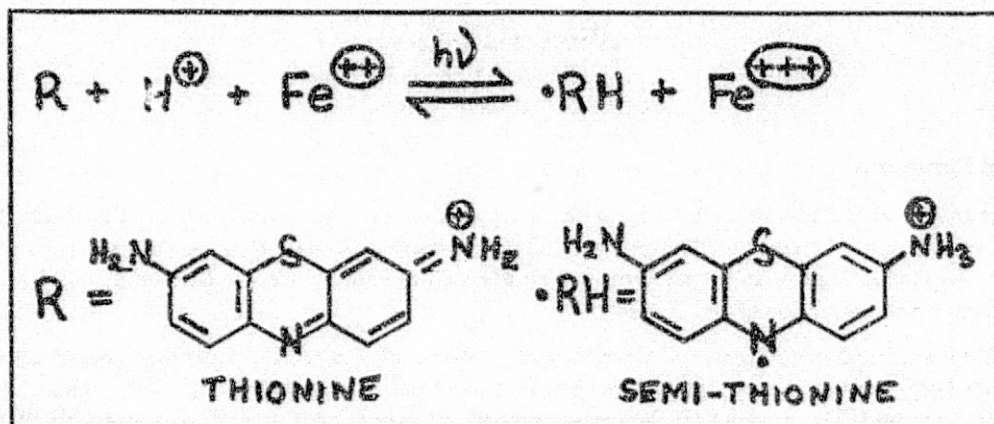


Fig. 1. Iron-Thionine System

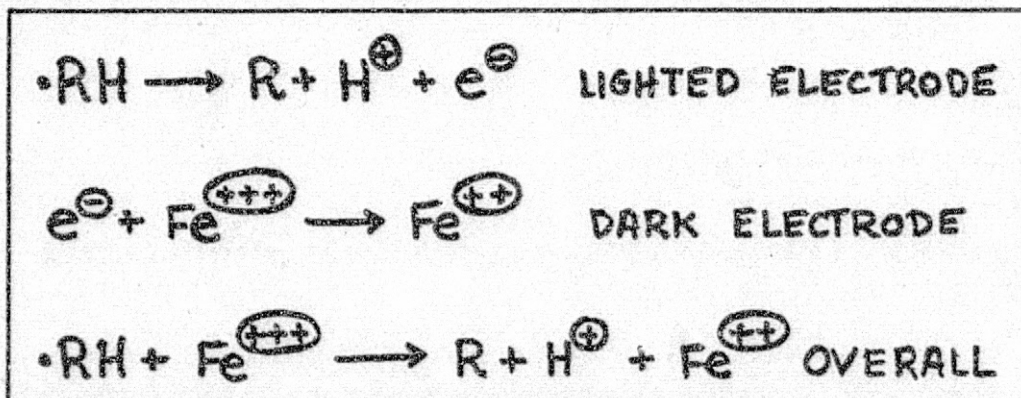


Fig. 2. Electrode Reactions

## ENHANCEMENT OF SELENIUM PHOTOVOLTAISM BY TREATMENT WITH PORPHYRINS

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### Presentation Summary

Porphyryns are any of several chemical structures derivable from a parent compound, porphin. Chlorophyll is a naturally occurring example of these materials. The solid-state possibilities of these molecules have been reviewed (Ref. 1). They are known organic semiconductors and photoconductors and have also been employed in model studies of organic superconduction (Refs. 2 and 3).

If the protective plastic coat is stripped from a commercial Se photocell and the surface is then coated with a layer or layers of various porphyryns by dipping into compressed monolayers on a Langmuir trough, both enhanced photo-voltages and photocurrents are obtained. If the layer is washed off with solvent, the effect is reversible (Table I). The magnitude of the enhancement varies with the porphyryn structure (cf. Table II) and also with the applied load, going through a maximum which varies for the particular conditions of study. Other dye structures lacking either the spectral or semiconductive characteristics of porphyryns do not produce this enhancement. Enhancements have remained permanent and stable for up to six months, so far. No dark voltages are observed and both forward and backward dark resistances are decreased. Comparable effects have been obtained on several Se cells and also on a Cu/CuO/Pb cell.

Although the dark resistance is decreased and although the structural variation shows that the porphyryn can act as a selective filter and radiation trap for the expected region of maximal spectral effect, neither of these mechanisms are sufficient to explain the large magnitude of the enhancement. Whether the mechanism involves photoeffects from the porphyryns themselves, modified surface recombination or conductivity, or functions by as yet unknown processes is still under study. Attempts are also under way to see if the effect can be extended to other types of photovoltaic cells such as Si and CdS.

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### Discussion

Q: I am a little puzzled. With a 1000 percent improvement in the selenium cell, you would have a cell which is between 20 and 30 percent efficient for solar energy conversion?

A: Not in this cell. This is not a good selenium cell. This is one of the cheap International Rectifier cells. Its efficiency was probably somewhere on the order of about one or two percent. Actually, we could make a guess at this; it might be increased to somewhere between about 8 and 12 percent by comparing it with a silicon cell.

Q: Does this mean it was equally good?

A: It was a little bit less efficient than the Centralab cells, so we guess it is somewhere between about 8 and 12 percent.

Q: What was the series resistance that you said these had?

A: This particular one I think was about 2000 ohms. We actually looked at the effect of loads — it goes through a maximum with loads. It also varies with the intensity of light. You get minimal effects at low light intensities, and at low intensity it was somewhat on the order of about 2000 ohms.

Q: What does this selenium cell look like when you start?

A: It's very simple. All you do is cut the plastic layer off of it. I had to spend a long time finding out what kind of proprietary material was on it and remove that so we could get at the barrier. It was zinc oxide in this particular cell. Then all we do is to dip it into a Langmuir trough. This is a monolayer of an organic material spread on a water trough, compressed until it is slightly more than a monolayer — just slightly collapsed. The selenium cell is dipped into it to pick up a monolayer of this material. The extensions are very, very high. It is one of the most strongly absorbing substances known.

Q: Where is it in the circuit?

A: It is essentially between the barrier layer and the collecting light ray. It is acting like the surface electrode. It does lower the dark resistance. It's on top of the cell. Yes, it's on top of the barrier layer.

Q: Do you put an electrode on top of that?

A: No. This particular cell has a collecting electrode only at one end. So essentially our porphyrin film is taking the place of the so-called transparent top electrode. It is taking the place of the zinc oxide.

Q: Do you scrape that off?

A: The layer itself has been a problem — taking it off without destroying the barrier layer. I might point out that with the semiconducting characteristics of the substance, this thing would have a very good surface conductivity — about an ohm-cm.

Q: For a monolayer?

A: Yes.

Q: Did you measure the V-I characteristic before you stripped the selenium cell and after you coated it?

A: Yes.

Q: Tell us how much the effect of a change of series resistance could have been.

A: It was of the order of about 20 percent for the forward resistance of this cell and something of the order of about 15 percent for the back current. It is not enough to account for the change. Although the index of the refraction is not known for these things, it is in the middle of the region of anomalous dispersion, so you can't make a simple filter trap calculation. Even if you take an enormous index of refraction, it wouldn't give you more than 20 percent.

Q: Will it work on silicon or CdS?

A: Yes. And that's what we are going to do next. A lot of people say to do the same with silicon. We'd love to do the same with silicon.

Table I. Control Experiments on International Rectifier Se Cell (B2M)  
With *ms*-Tetraphenylporphin, Ambient Light, and 2500-Ohm Load

Conditions	Volts (mV)	Current ( $\mu$ A)	Power ( $\mu$ W)
Cell with protective plastic coat	36	14	0.504
Cell with coat scraped off	20	8	0.160
Cell with one layer of TPP*	32	12	0.384
Cell with TPP washed off with $\text{CHCl}_3$	21	8	0.168
Cell recoated with TPP	40	16	0.640
Cell re washed with solvent	20	8	0.160
Cell recoated with one layer	40	16	0.640
Cell coated with second layer	42	17	0.714
Cell coated with third layer	42	17	0.714
Cell heated with heat gun lightly	50	20	1.000
Cell cooled with heat gun to ambient	42	17	0.714
Cell coated with fourth layer	40	16	0.640
Cell washed with solvent	21	8	0.168

\*TPP = *ms*-tetraphenylporphin.

Table II. Effect of Porphyrin Structure on Enhancement of Se Photovoltaism of B2M Cell

Treatment	Maximum			Percent Increase from Fiducial
	Volts (mV)	Current ( $\mu$ A)	Power ( $\mu$ W)	
Fiducial	21	8	0.168	-
TPP	42	17	0.714	425
CuTPP	46	18	0.828	492
MgTPP	49	19	0.931	555
AgTPP	50	20	1.000	595
SnTPP $Cl_2$	53	21	1.113	663
FeTPP $Cl$	50	20	1.000	595
ZnTPP	50	20	1.000	595
ZnOEP	40	16	0.640	380
T(pCN)PP	50	20	1.000	595
T(nPr)P	55	22	1.210	720
Porphin	48	18	0.864	515
TPC	55	22	1.210	720
TPPH $_2^{+2}$	65	26	1.690	1000

TPP = *ms*-tetraphenylporphin; MTPP = metallo-TPP; OEP = octaethylporphin; T(pCN)PP = *ms*-tetra(*p*-cyano) phenylporphin; T(nPr)P = *ms*-tetra(*n*-propyl) porphin; TPC = *ms*-tetraphenylchlorin; TPPH $_2^{+2}$  = acid salt of TPP.

## SEMICONDUCTOR-ELECTROLYTE PHOTOVOLTAIC ENERGY CONVERTER

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## Presentation Summary

We believe that efficient, economical photovoltaic solar energy converters may be realized in an electrolyte-semiconductor system. Semiconductor electrode reactions and photoelectric phenomena have been studied for many years. The modern phase of these studies dates from the work of Brattain and Garrett on Ge in 1955 (Ref. 1). However, very little work seems to have been done to evaluate the technical importance of the phenomena for energy conversion. At least one patent has been issued for a Si-H<sub>2</sub>SO<sub>4</sub>-Pt electrolytic solar cell (Ref. 2), but Si is a poor choice of semiconductor because of its small energy gap and weak, indirect absorption edge.

We have been led to this area of research as a result of some observations on the photo response of a CdS-0.02 M KCl in CH<sub>3</sub>OH cell. The remarkable result of unity short-circuit quantum efficiency was observed for photon energies greater than the bandgap energy of CdS. This result is shown in Fig. 1. In a cell with a different electrolyte, an open-circuit voltage of 0.8 volt was obtained. We will briefly describe the phenomena involved and the problems to be solved for energy conversion.

In Fig. 2 we show the upward surface band bending of an n-type semiconductor in contact with an oxidizing electrolyte. Photo generated hole-electron pairs in the surface space charge region are separated by the electric field in the space charge layer, leading to the surface photo voltage (Ref. 3).

1. For good short-circuit current quantum efficiency, it is necessary that the incident light be strongly absorbed in the surface space charge layer; i.e.,

$$\alpha \geq \frac{1}{W} \text{ cm}^{-1}$$

where  $\alpha$  is the absorption coefficient of the semiconductor. This indicates the requirement of a lightly doped,  $n \sim 10^{15} \text{ cm}^{-3}$ , direct gap semiconductor.

2. The surface band bending  $V_{SC}$  should be maximized since this represents the maximum possible open-circuit voltage obtainable under high illumination conditions.  $V_{SC}$  is determined by the particular semiconductor and electrolyte pair, and the electrochemical reactions occurring as a unit charge is carried around the circuit as described in the appendix.

3. The energy gap of the semiconductor must be chosen to match the solar spectrum (Ref. 4). The maximum band bending is less than  $E_g$ ,

$$V_{SC} < E_g$$

while the solar photon flux which may be absorbed,  $\phi (h\nu > E_g)$ , is a monotonically decreasing function of  $E_g$ . There is thus a theoretically optimum value of  $E_g$ .

4. The electrochemical reaction involved in charge transport across the semiconductor-electrolyte interface must be nondestructive of the semiconductor surface and, preferably, not consume electrolyte unless a useful product is produced.

5. Electrode overpotentials must be minimized. This is a significant problem in fuel cell technology which is very analogous to the device under consideration.

6. Electrode and electrolyte resistance must be minimized. This is the well-known problem of electroding a solar cell to minimize series resistance of the device. Some possible cell configurations are shown in Fig. 3.

A review of the literature on semiconductor electrochemistry has been made. Some of the salient features of this search are summarized below.

The first work on CdS was by Williams (Ref. 5), who studied the photovoltaic effect with an aqueous KCl electrolyte. Since then, some work has been done with various electrolytes including some redox systems (Refs. 6-9).

While CdSe was considered in some of the papers along with CdS (Refs. 7, 10), only one paper appears to have been published dealing with CdTe (Ref. 11). This paper reports observations identical to our experiments on CdS in that the photovoltage is due to photo pair generation and charge separation both occurring in the surface depletion region.

The most extensive work in this field appears to have been done by Professor H. Gerisher and his students. Some of this work has been referred to above. In addition, he has written a number of excellent review papers on the subject (Refs. 12-15). However, there does not appear to have been any work on the possible technical utilization of the semiconductor-electrolyte system as a practical energy conversion device.

Finally, we comment on the potential economical construction of this type of solar cell. The mechanism involved in this cell does not require the use of a single crystal material as in the Si solar cell (to obtain long minority carrier diffusion lengths). Thus significant material requirements are a semiconductor thickness of a few reciprocal absorption constants and a reasonably low carrier concentration ( $n \sim 10^{15} \text{ cm}^{-3}$ ). Therefore, structures using an evaporated (Ref. 16), sputtered (Ref. 17), flash evaporated (Ref. 18), or anodically grown (Ref. 19) semiconductor film are feasible.

## Appendix

## Development of the Space Charge Voltage

Development of the open circuit photovoltage and surface band bending  $V_{SC}$  may be understood by reference to Fig. 2. The energy added to the system by absorption of one photon of energy  $h\nu = E_g$  required to create one hole-electron pair is dissipated by:

$$h\nu = E_g = V_{SC} + V_{Helm} + E_f + \frac{\Delta G}{F} + IR + \Delta E_s + \alpha(I) \quad (A-1)$$

where

$V_{SC}$  = energy dissipation in charge separation in space charge layer

$V_{Helm}$  = potential drop across Helmholtz layer

$E_f$  = energy loss of electron in transfer from conduction band of semiconductor to Fermi surface in metal (ohmic contact to semiconductor assumed)

$\frac{\Delta G}{F}$  = free energy of electrode reactions normalized to one unit of charge transfer

$IR$  = ohmic losses in external conductor and electrolyte

$\Delta E_s$  = other entropy producing processes (such as change of the solvation structure around redox ions)

$\alpha(I)$  = electrode over potentials

Under open-circuit conditions

$$V_{SC} = E_g - \frac{\Delta G}{F} - E_f - V_{Helm} - \Delta E_s \quad (A-2)$$

$E_g$  is determined by the particular semiconductor used. Unfortunately, minimizing  $E_f$  conflicts with the requirements of a large space charge width  $W$ , since

$$E_f = \frac{kT}{q} \ln \frac{N_C}{N_D} \quad (A-3)$$

where

$$\begin{aligned} N_C &= \frac{2}{h^3} (2\pi kTm^*)^{3/2} \\ &= 2.5 \times 10^{19} \left( \frac{m^*}{m_0} \right)^{3/2} \text{ cm}^{-3} \end{aligned} \quad (A-4)$$

at  $T = 300^\circ\text{K}$ .

Unlike the metal-electrolyte contact, the voltage drop across the Helmholtz layer in the semiconductor-electrolyte contact is a negligible fraction of the voltage across the double layer. Almost the entire voltage drop occurs across the semiconductor space charge layer.



An example of other entropy producing processes which might contribute to  $\Delta E_s$  in Eqs. (A-1) and (A-2) is the change in structure of the solvation shell around the ions of a redox electrolyte when a change of oxidation state occurs.

The principal contribution to  $V_{SC}$  will be the electrode reactions which determine  $\Delta G$ . In our preliminary work on the CdS electrode we have used the following electrolytes:

0.04 M  $KNO_3$  in N-methylacetamide ( $CH_3CONHCH_3$ )

0.04 M  $KNO_3$  in  $CH_3OH$

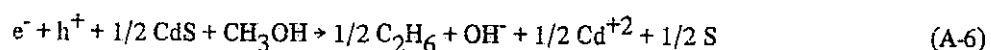
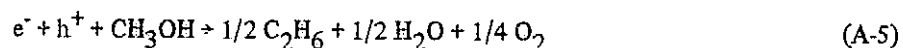
0.02 M  $KCl$  in  $CH_3OH$

0.2 M  $KOH$  in  $CH_3OH$

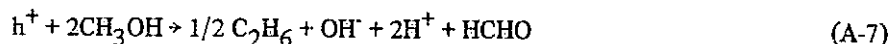
1.0 M  $KOH$  in  $H_2O$

We have not yet studied the electrode reactions in detail, but we can give some reasonable hypotheses.

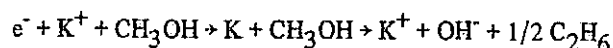
For  $KOH$  in  $CH_3OH$ , there are three obvious overall cell reactions



or



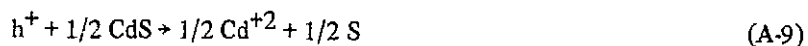
The cathodic half-cell reactions are identical in all cases



but the anodic half-cell reaction for Eq. (A-5) is



For Eq. (A-6)



and for Eq. (A-7)



For reactions (A-5), (A-8) we have evolution of  $O_2$  at the anode while for reactions (A-6), (A-9) we have dissolution of the CdS surface. Reactions (A-7) and (A-10) result in a current doubling as formaldehyde is produced from methanol.

In Fig. A-1 we show the free energy variation with temperature for two competing anode reactions. Using the criteria suggested by Williams (Ref. 5) that the reaction requiring the lowest free energy should dominate, we note the transition from one reaction to the other at  $75^\circ C$ . For  $T > 75^\circ C$ , the electrolyte is consumed with the evolution of  $O_2$ , while for  $T < 75^\circ C$ , electrode dissolution should occur with  $Cd^{+2}$  going into solution and a buildup of free S on the electrode surface.

Unfortunately,  $T = 75^{\circ}\text{C}$  is above the boiling point of  $\text{CH}_3\text{OH}$  at atmospheric pressure. However, similar reactions occur in  $\text{H}_2\text{O}$  but require a much larger change in free energy  $\Delta G/F$ , which will reduce the cell voltage as indicated in Eqs. (A-1) and (A-2).

Initial research should involve a study of possible electrolytes which will maximize  $V_{\text{SC}}$  without electrode dissolution. The two techniques we have used for measurement of  $V_{\text{SC}}$  are open-circuit photovoltage and zero intercept of a  $1/C^2$  vs  $V$  plot. The latter measurement can also be used to obtain the carrier density  $n$  in the semiconductor. An example of this type of measurement for CdS in 1M KOH:H<sub>2</sub>O electrolyte is shown in Fig. (A-2). This particular crystal was characterized by  $N_{\text{D}} = 1.5 \times 10^{17} \text{ cm}^{-3}$  and from the  $1/C^2 = 0$  intercept,  $V_{\text{SC}} = 0.825$ , while an open-circuit photovoltage of  $V_{\text{OC}} = 0.62$  was measured. ( $V_{\text{OC}}$  could be shifted to 0.8 volts by buffering the KOH with acetic acid.)

Electrolyte selection must also involve consideration of electrode dissolution, surface state, and overvoltage problems. Some redox systems appear promising.

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### Discussion

- Q: The previous experiment with cadmium sulfide-electrolyte solution showed that with an n-type semiconductor, when you have oxygen evolution at the electrode, you do have a decomposition of the CdS electrode. Would you employ that in your electrochemical cells?
- A: Yes. When we used water we did observe decomposition with the only two aqueous-based electrolytes we used. We did observe deterioration of the cadmium sulfide surface. And probably – we haven't done all of the chemistry yet, so we don't really know what is being produced – oxygen was evolving. When we were using the methanol electrolyte, our best guess is that we were producing formaldehyde, with the KCl as the salt branch. For KCl in methanol, there was no observed deterioration of the surface. When we used potassium hydroxide in methanol we did observe some surface deterioration. This is where the research should be done at the moment: the charge-transfer mechanism across the semiconductor-electrolyte interface.
- Q: Any estimates about efficiencies of such processes?
- A: By doing our radiometry (and our thermocouple could be calibrated a little better) we are observing greater than unity short-circuit quantum efficiency. This is to be expected because there was a charge-doubling reaction that went on at the surface in producing the formaldehyde from methanol. So, in other words, you should not be surprised to see this approach with some of our other electrolytes. The open-circuit voltage should be determined by the bandgap of the semiconductor and the chemical-electrochemical reaction at the surface. We have observed an open-circuit photovoltage of cadmium sulphide of 0.8 V. So I would suspect that we should be able to approach the calculated theoretical efficiencies of the semiconductors based on bandgap considerations.
- Q: Do you use single crystals for ---?
- A: This was single crystal work simply because we had single crystals. We looked at both the sulphur face and the cadmium face, observing no significant difference in behavior. I see no reason for single crystals being needed, and obviously we are interested in the effect on thin films of the semiconductors.
- Q: But you still have the question of diffusion length to contend with?
- A: Yes, we have the question of diffusion length to contend with. But the charge separation takes place in the high-field space-charge region. So we hope for a hole-electron pair generated within 0.5 microns of the surface; according to the absorption coefficient of  $2 \times 10^4 \text{ cm}^{-1}$ , we should be able to get effective charge separation before recombination.
- Q: How does the resistance of the solution figure into this?
- A: The resistance of the solution figures into this in that I didn't show you a V-I characteristic. This is partially an artifact of the electrode geometry that we are dealing with. Of course, we had proposed, or had thought of various electrode configurations which would minimize the series resistance of the cell. And if you go to

something like an egg crate, you can reduce the resistance by increasing the height of the top of the egg crate to the bottom of the egg crate above the semiconductor surface. So that there are various electrode configurations that one could ---.

Q: What was the observed efficiency?

A: I can't give you an observed efficiency because we didn't measure one. The crystal was about 0.07 square centimeters exposed area and the cell series resistance was about 5 to 10 thousand ohms with the electrolyte concentrations and electrode configurations we were dealing with. So if you want to figure that out, you can consider a unity quantum efficiency, open-circuit voltage typically of six tenths of a volt.

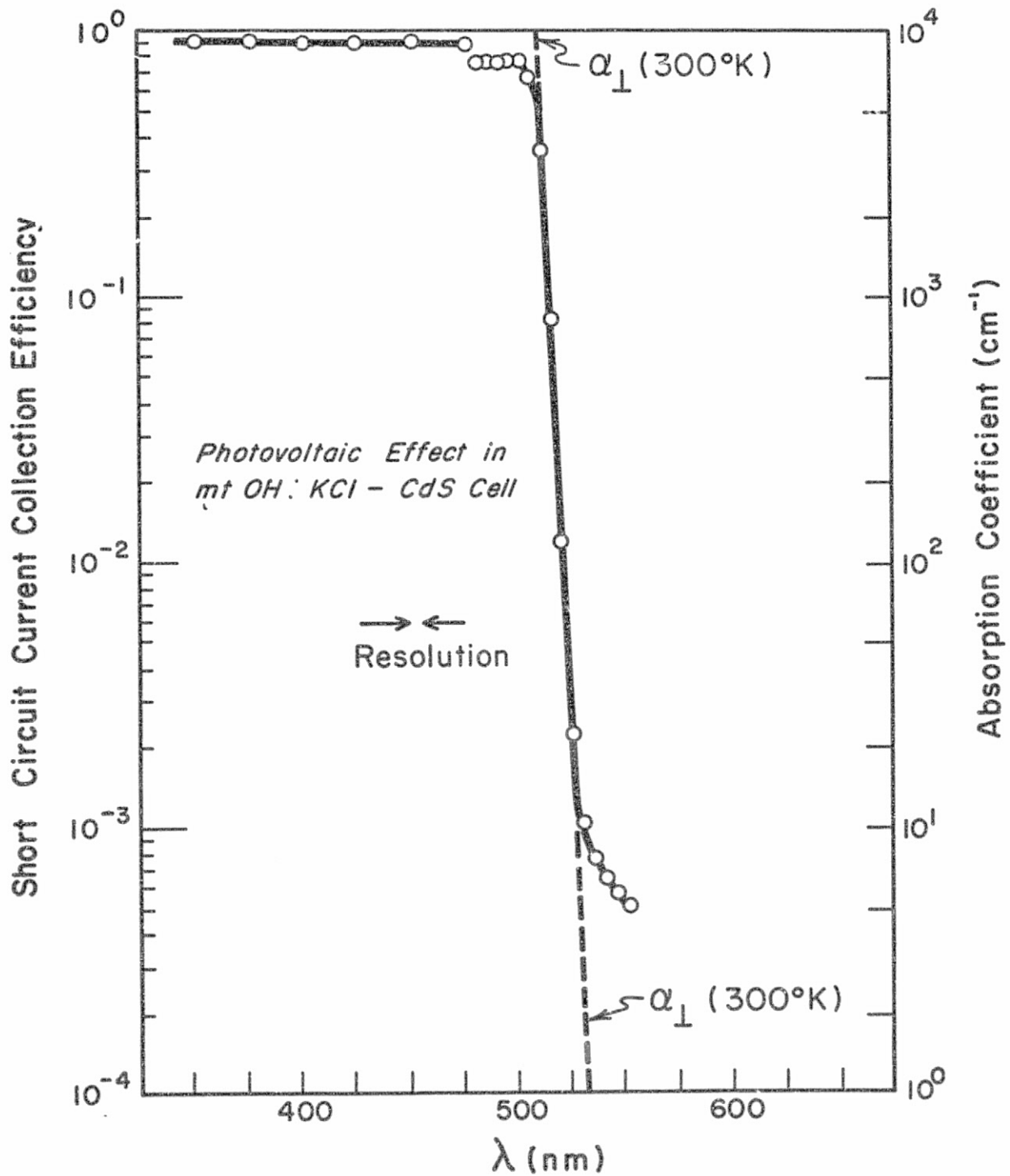


Fig. 1. Short-Circuit Photovoltaic Current from CdS: Electrolyte Cell

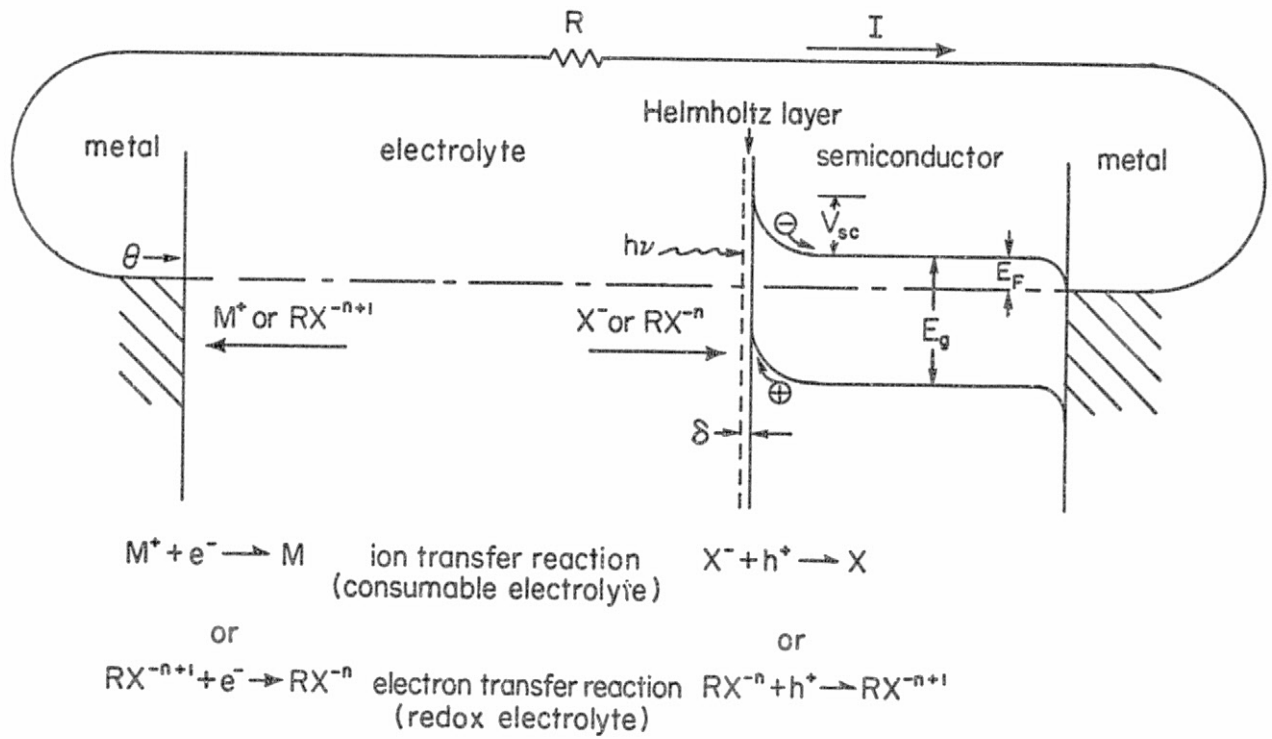


Fig. 2. Processes in Electrolyte-Semiconductor Photovoltaic Cell

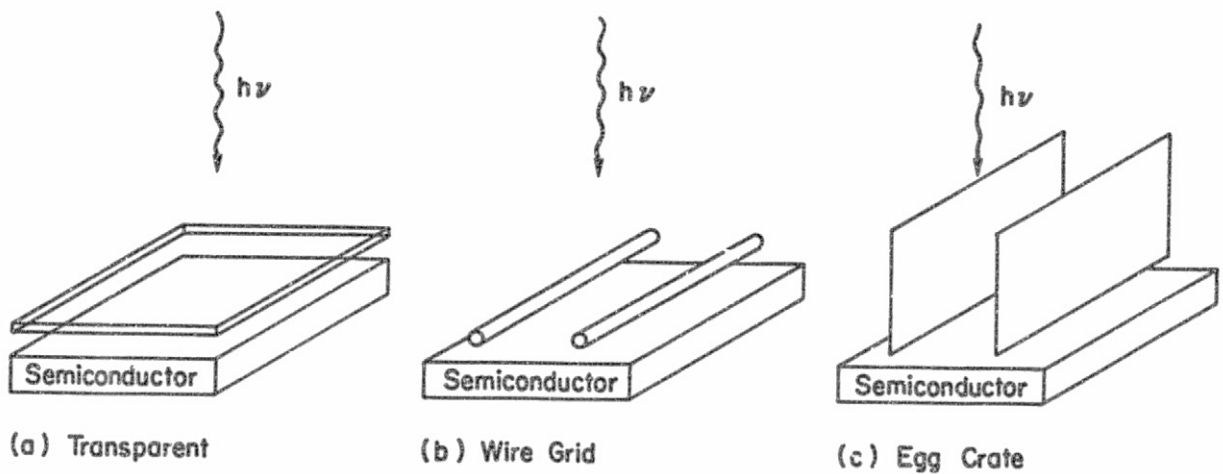


Fig. 3. Electrode Configurations for Semiconductor-Electrolyte Photovoltaic Cell

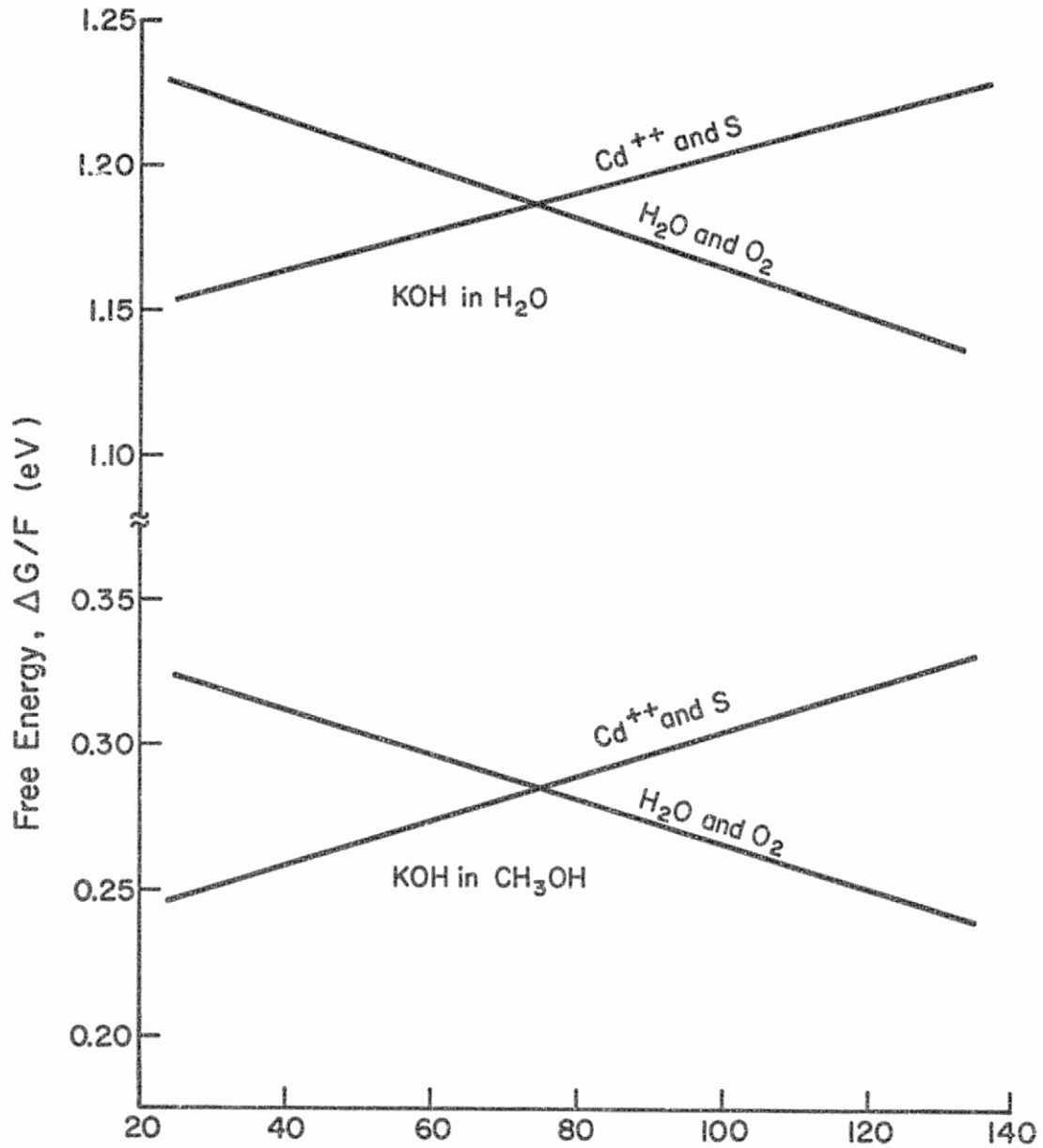


Fig. A-1. Free Energy Variation with Temperature for Two Possible Anodic Reactions at CdS Electrode

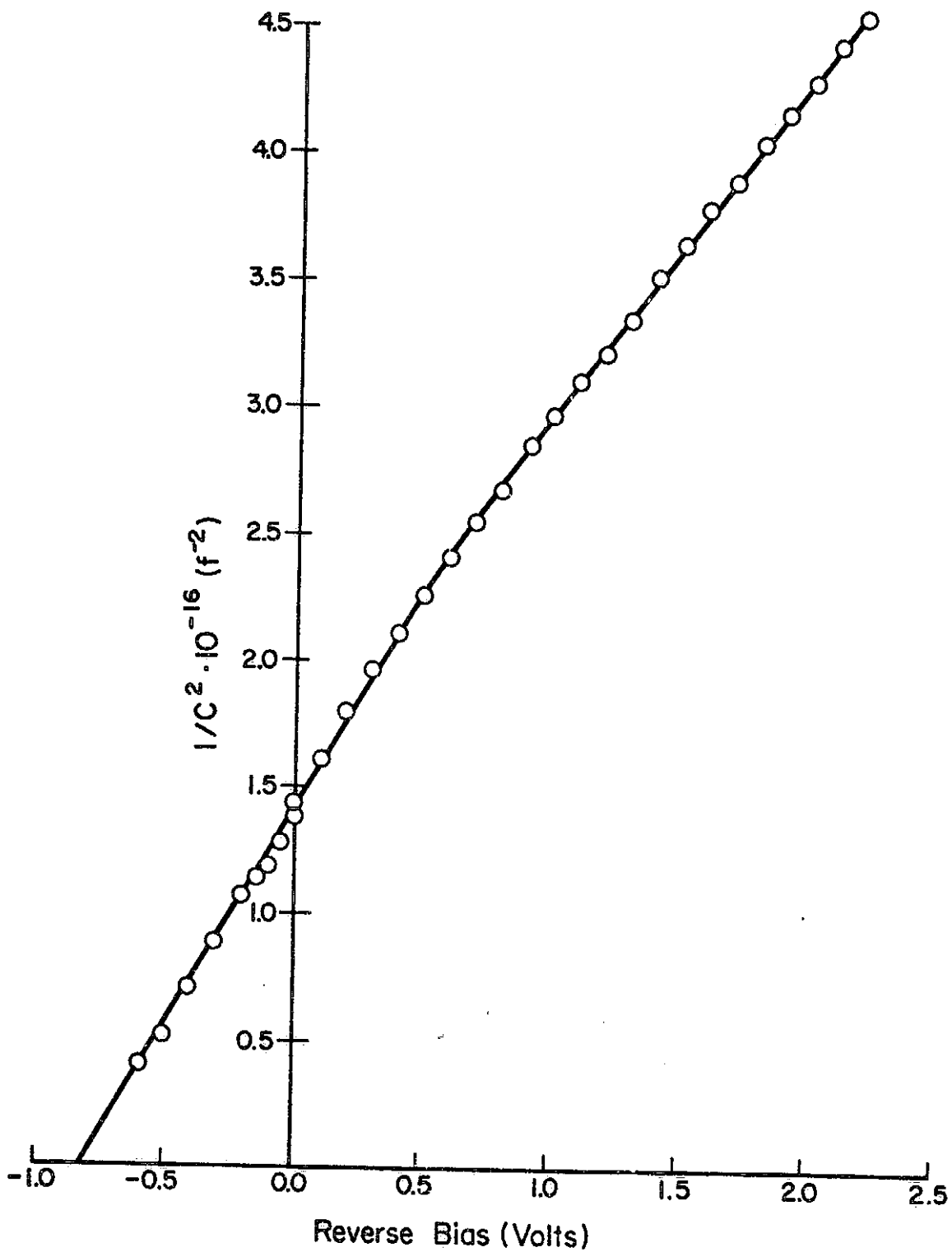


Fig. A-2. Schottky-Mott Plot for CdS in 1M KOH



## CONVERSION OF SOLAR ENERGY USING PHOTOSYNTHETIC MEMBRANES

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### Presentation Summary

The photovoltaic effect in photosynthetic membranes (bimolecular lipid membranes containing photosynthetic pigments) is well known. Experiments designed for studies of photosynthesis and other membrane-related phenomena have shown that an e.m.f. is produced when the membrane is illuminated by an artificial light source (Refs. 1 and 2). The light-induced electrical effect has been explained in terms of charge carrier production and separation, as electrons and positive "holes" are generated in the membrane (Ref. 3). A schematic illustration of the basic electronic process in the membrane is shown in Fig. 1. The close resemblance of such a charged membrane and the P-N junction in a semiconductor device (e.g., doped silicon) is clearly evident. It suggests that the photosynthetic membrane can be used as a barrier layer in a photovoltaic cell to convert light energy (or solar energy) to electrical power.

Based on this idea, an experimental device, shown in Fig. 2, was constructed and tested in our laboratory. The bimolecular lipid membrane, containing oil-soluble chlorophyll, was formed on a small hole (~1.5 mm) drilled in a thin Teflon sheet. The Teflon sheet served as a partition separating the test chamber into two compartments. These compartments were filled with aqueous buffer solutions (0.1 M acetate) containing  $\text{FeCl}_3$  ( $10^{-3}$  M) and 1,4 dihydroquinone. A low power (1 mW) helium-neon lasers (wavelength: 6328 Å) was used as the light source for the experiment. The light-induced photoelectric effects were detected by using a pair of platinum electrodes.

Preliminary experimental results indicated that an open-circuit membrane potential greater than 100 mV could be achieved. A small net power output (~0.1 mW/cm<sup>2</sup> of the membrane area) from the illuminated membrane was obtained by using an external load resistor. Indications are that both the membrane potential and the power output can be greatly increased by properly adjusting factors affecting the electronic transfer process in the membrane cells. Some of the major factors include:

- (1) Physical configuration and chemical constituents of the membrane.
- (2) Compositions of the bathing electrolyte solutions.
- (3) Types of electrodes.
- (4) Interfacial conditions at the membrane-solution and solution-electrode interfaces.
- (5) Intensity and wavelength of the light source.

At present there is no quantitative information available as to the photoelectrical conversion efficiency of the photosynthetic membrane. Estimate based on the photosynthesis efficiency of green plant indicates that 30 to 50% of the incident light energy can be converted to electrical power. The utilization of solar radiation by the photosynthetic pigment is believed to be limited to the short wavelength portion of the solar spectrum, or about 50% of the total solar radiation. Thus, the overall solar energy conversion efficiency by the photosynthetic membrane would probably be in the range of 15-25%. If these estimates were correct, the membrane cells would be more efficient than existing photovoltaic cells made of semiconductor materials (e.g., the best silicon cell has a maximum solar energy conversion efficiency of 14%) (Ref. 4).

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## Discussion

- Q: You said you wanted to attach an electrode directly to the membrane, any suggestions on this?
- A: Yes. We have some ideas we have not tried yet. We hope we can make micromembranes with either pole, but making the surface, of course, be the conductor of energy. One of the thoughts that we have in mind is to polymerize the surface. If we can polymerize a layer of the surface, we can make it conductive.
- Q: What can you tell us about the efficiency of the photosynthesis process? I have the impression that the silicon solar cells are more efficient.
- A: I think there is some literature indicating that photosynthesis (the light received by the leaves which converts the chemical bonds) and these efficiencies were isolated losses which are not really in the pigment – the photosynthetic efficiencies can be as high as 15 to 25 percent. Now, this is – I'm quoting somebody else's work – I have no idea what that efficiency term means, but the indications are they may be efficient.
- Q: That's not over the whole solar spectrum?
- A: No. Because only about 40 to 45 percent of the spectrum is absorbable by the pigment, somewhere between 700 down to about 400 nanometers.
- C: May I read a report from Robert Clayton, who is an expert in this area? "The maximum efficiency with which solar energy in the field is converted to stored energy in either higher plants or in tanks of algae is about 3 percent."
- A: Yes, you have to take into account of all of the environmental factors, too, I guess. The nutrition problem and all of these problems. Algae under controlled conditions have shown efficiencies of up to 20 percent – in the laboratory, not in their natural state.
- Q: Have you attempted to measure such things as lifetimes and excited states in these membranes?
- A: No, we have not at this time. We hope we will.

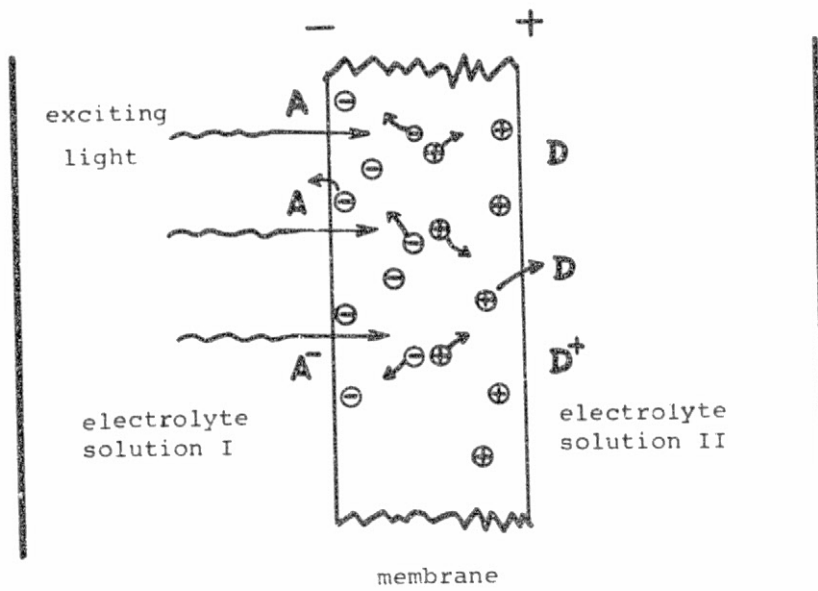


Fig. 1. Principle of Photovoltaic Effect in Bimolecular Lipid Membrane Containing Photosynthetic Pigment: A = Electron Acceptor; D = Electron Donor;  $\ominus$  = Electron;  $\oplus$  = Positive Hole

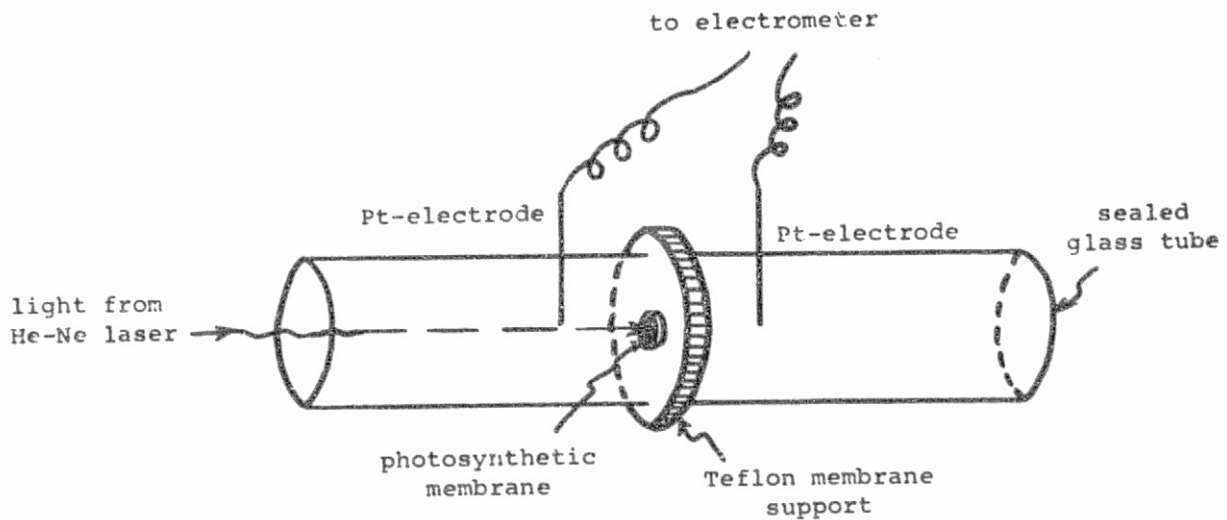


Fig. 2. Apparatus for Studying Photovoltaic Effect in Photosynthetic Membranes

## ELECTRON-BEAM EVAPORATION OF SOLAR CELL MATERIALS

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### Presentation Summary

We have developed a system for electron-beam evaporation of compounds. The vacuum system has an electrode and grounding arrangement to minimize the electric field produced by the electron-beam gun. This arrangement of electrodes minimizes the separation of ions which may be produced when the compounds are produced. In addition, a gas jet is used on the heated substrate to add atoms which might be lost on evaporation. Figure 1 is a diagram of the evaporation system.

We have evaporated  $Al_2O_3$  on silicon and GaAsP with properties suitable for transistor gate material. The  $Al_2O_3$  on silicon transistors give good characteristics.

As an example of compound semiconductor evaporation, we have used indium antimonide.

The metal masks and substrate glass were degreased and cleaned ultrasonically in solvents, and positioned above the crucible at a distance of 5 inches. A thermocouple was placed touching the surface of the substrate and was connected to a digital voltmeter. The substrate heater with molybdenum reflector (quartz-iodine lamps) was placed at a distance of 2.5 to 3.0 inches from the substrate, heating it uniformly. A thickness monitor sensor was fixed near the substrate.

With the vacuum system pumping, the substrate was heated to 400°C for 30 minutes for outgassing and cooled down to ~300°C. When the pressure was  $3 \times 10^{-7}$  to  $5 \times 10^{-7}$  torr, a controlled amount of InSb charge was evaporated with the electron-beam gun at a rate of 200 to 300 Å/sec. The samples were cooled to room temperature before being removed from the vacuum system and then heated in an oven at 250°C for 20 to 30 minutes to form a protective oxide layer.

The InSb films with protective oxide layer were recrystallized in a furnace which provides a mass production capability as opposed to the electron-beam micro-zone melting that allows processing of individual items only. Pre-purified dry argon was passed over the samples at a rate of 1.5 to 2.5 liters/min. The temperature of the furnace was maintained between 525 and 535°C; recrystallization time varied from 3 to 4 minutes. Then the samples were pulled to the end of the tube to allow slow cool-down. These samples were etched in concentrated HCl acid to remove excess indium from the film surface, and then indium contacts for Hall measurements were made with an ultrasonic soldering iron.

The resulting Hall effect devices showed mobilities up to 75,000  $cm^2/V\text{-sec}$  at room temperature. The mobilities are essentially equal to or better than normal bulk mobilities of the original material.

This method offers promise for the electron-beam evaporation of solar cell materials.

### Discussion

Q: What was the substrate material?

A: We tried a number of different substrate materials. Glass seemed to work as well as anything, at least if we went to a 3-micron thickness. The substrate had some effect if you stayed with very thin films.

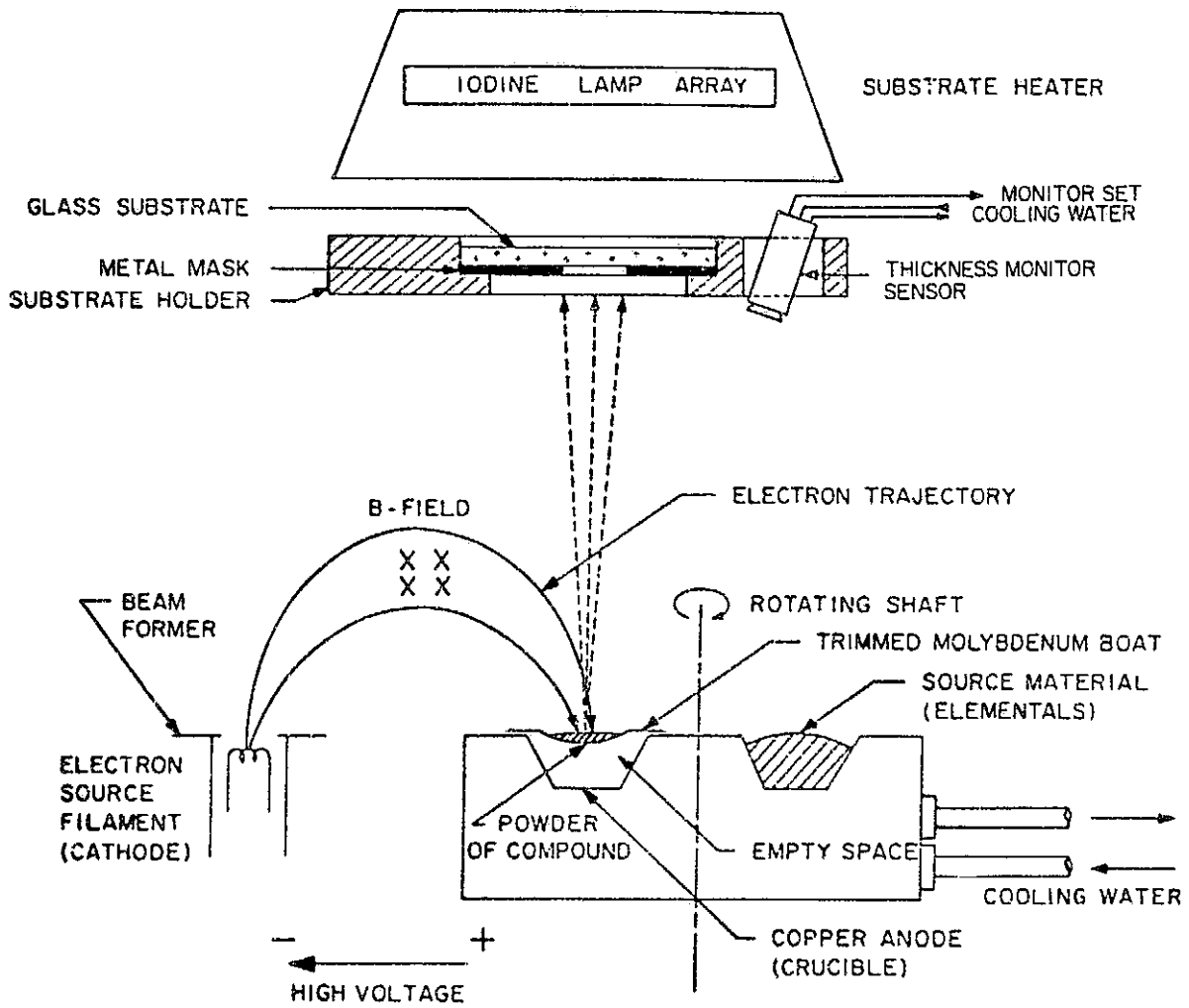


Fig. 1. Setup for Electron Beam Evaporation

## PIN HETEROJUNCTION SOLAR CELLS

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**Presentation Summary**

The use of PIN heterojunctions of direct band gap semiconductors can in principle circumvent a number of the problems that exist in silicon solar cells. Such devices have received little attention in the past because of their inherent complexity and the fact that applicable semiconductors are not as well characterized as silicon.

What is envisioned is a base layer of a narrow band gap semiconductor heavily doped p-type, followed by a close to intrinsic layer of the same material and finally a wide band gap top layer heavily doped n-type. Radiation within the spectral window set by the band gap differences of the materials penetrates the surface layer and is absorbed in the intrinsic region of the device. The strong electric field present in the intrinsic region separates the electron hole pairs, excited by the absorbed radiation, delivering the holes to the p-type base layer and the electrons to the n-type surface layer.

Such a device has the inherent characteristic of decoupling the collection efficiency from the series resistance. Both the base and top layers can be made highly conductive for low series resistance without adversely affecting the carrier lifetime in the intrinsic layer. It can be shown that high surface recombination velocities which strongly affect collection efficiencies in silicon cells play only a minor role in this device. In the intrinsic layer, the generation rate  $G(x)$  is related to the current density  $J(x)$  by

$$G(x) = \frac{\partial J(x)}{\partial x} \quad (1)$$

Integrating equation (1) and considering only the holes which are being field driven away from the heterojunction,

$$J_h(0) - D_P \frac{\partial P}{\partial x} - v_D P = I_0 (1 - e^{-\alpha x}) \quad (2)$$

where  $J_h(0)$  is the surface recombination hole current at the heterojunction interface,  $D_P$  the diffusion constant for holes,  $P$  the hole concentration,  $v_D$  the drift velocity for holes,  $I_0$  the intensity of the incoming radiation,  $\alpha$  the absorption coefficient for the intrinsic layer, and  $x$  the distance as measured from the junction. If one assumes an infinite recombination velocity for holes at the junction, zero recombination in the bulk of the intrinsic layer, and neglects the homogeneous solution of equation (2) (since this is essentially the forward biased diode current), one finds that

$$J_h(0) = \frac{D_P}{v_D + D_P} \quad (3)$$

The collection efficiency  $Q$  is then given by

$$Q = \left( 1 - \frac{J_h(0)}{I_0} \right) \gamma \quad (4)$$

where  $\gamma$  is the fraction of light absorbed in the intrinsic region to that incident on it. Combining equations (3) and (4),

$$Q = \frac{\gamma}{1 + \frac{\alpha D_P}{\nu_D}} \quad (5)$$

Substituting for  $D_P$  and  $\nu_D$ ,

$$Q = \frac{\gamma}{1 + \frac{\alpha k \Gamma / e}{E}} \quad (6)$$

where  $k \Gamma / e$  is the thermal energy in volts and  $E$  is the electric field in the intrinsic region. For representative values  $\alpha = 10^4 \text{ cm}^{-1}$ ,  $E = 5 \times 10^3 \text{ volts cm}^{-1}$  and intrinsic layers of three microns in thickness, collection efficiencies of over 90% exist. Forward biasing the diode to half the band gap voltage results in less than a 4% reduction in collection efficiency. The assumption that recombination in the bulk is negligible is based on comparing transit times with carrier lifetimes. This transit time for a 1.5-eV band gap material with the dimension above is  $10^{-9}$  seconds. For carrier lifetime as short as  $10^{-8}$  seconds, bulk recombination is negligible. The  $\gamma$  factor can be traded off with transit time by reducing the thickness of the intrinsic layer. Such reductions appear twice in the transit time calculation, thus a factor of four change in layer thickness has the effect of reducing the transit time by a factor of sixteen.

Although the possibility of achieving close to theoretical efficiency is enhanced in these devices, the cost-power ratio is a more significant factor. Cells of CdTe-ZnSe have theoretical efficiencies in the 25% range. The materials required have a reasonable abundance. Because of the partially ionic nature of the crystals, it may be possible to sputter deposit polycrystalline layers without severe degradation of the conversion efficiency. For a 10-micron CdTe base plus intrinsic layer and a 100-micron ZnSe top layer, the cost of the materials including a gold-coated aluminum substrate and a grided top electrode of indium is approximately \$30 per square meter. This is based on the use of 99.999% pure starting materials. It is estimated that the cost of processing the devices in a continuous fashion would add another \$20 per square meter to the price. The major questions that must be resolved are associated with degradation of lifetime and the effect of traps on device efficiency. Polycrystalline films are known to degrade from single crystals in this fashion. The longer wavelength incident radiation may reduce the detrimental effect of traps in the intrinsic layer. Degradation of lifetime can to some extent be compensated by making the intrinsic layer thinner. Should the overall efficiency be maintainable at the 5% level, the cost-power ratio would come in at \$1000 per kilowatt.

### Discussion

- Q: Why is series resistance not important, since we have to have the current flowing through the entire circuit?
- A: The series resistance can be made as low as you want it to be made. The series resistance comes about from two regions—the surface region and the base region. There is no series resistance associated with the i-layer at all—that's the generator.
- Q: The metal contact?
- A: The surface layer here was made 100 microns thick; it was zinc selenide 0.01 ohm centimeters, n-type. That's not going to create a contact problem. The problem lies in the series resistance when you put a p-n junction together, and you have carrier lifetimes in the material versus series resistance. If you start making it very conductive, the carrier lifetime goes way down and then there is no collection efficiency. Here, the carrier lifetime problem is associated with the center region which is your generator, rather than with the contact regions—the base layer or the top layer; thus the series resistance effectively is kept down by keeping the conductivity of both the surface wide bandgap semiconductor and the base p-type layer extremely low. There is very little series resistance there.
- C: The open-circuit voltage is the difference between minority quasi-Fermi levels; so if you heavily dope in the righthand side and in the lefthand side, you somewhat counteract the ability to spread the quasi-Fermi levels, and there will be some limitations. Otherwise this is a good idea.
- C: Well, there are some limitations.
- C: Right. So it sounds great if one can still manage to get the quasi-Fermi levels separated. Although you said the lifetimes of your carriers in the i-region are high, your open-circuit voltage is limited by not overdoping the p and n range too much. So conductivity on one side and minority carrier lifetime and quasi-Fermi level on the other side require tradeoff.
- A: Yes. There are still tradeoffs that you have to worry about. I might mention that you have to keep about a one-volt energy gap difference between the base layer and the top layer in order to get reasonable efficiencies.
- Q: Why is this? In the sense that it is the high bandgap material which is receiving the light?
- A: It passes through—that's a window. This is like 2.6 electron volts in the zinc selenide. So everything between, say, 1.44 for cadmium telluride and 2.6 is going to get by here, and that gives you reasonable theoretical, like in the 25 percent range. If everything worked out right, you would have some 25 percent.
- Q: What's the transparency of heavily doped zinc selenide?
- A: Below the gap? It's extremely good, about 99 percent.
- Q: Is this heavily doped?
- A: Right. When you say heavily doped, it depends upon what you mean. If you are talking about  $10^{19}$  carriers per  $\text{cm}^3$ , you have no problems.
- Q: The conductivity is what?
- A: It is 0.01 ohm-centimeters. Usually what they do is to dope the zinc selenide. You build in zinc vacancies and doping produces higher conductivities.



## PHOTOVOLTAIC SOLAR ENERGY CONVERSION USING HIGH-TEMPERATURE THERMAL RESERVOIRS

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### Presentation Summary

A new technique is proposed for photovoltaic generation of electricity from solar energy which involves storage of the solar energy in high-temperature thermal reservoirs. The two main advantages of the system are (1) a potential for achieving a substantially higher efficiency than is possible in direct photovoltaic conversion and (2) economical energy storage. With 24-hour storage, theoretical efficiencies of about 32% can be achieved in a system which could be constructed at an estimated cost of \$1100/kW. Development of efficient and economical  $Pb_{1-x}Cd_xS$  photovoltaic cells with infrared cutoff wavelengths appropriate for this scheme appears feasible.

As shown in Fig. 1, concentrated input solar radiation passes through a heat-mirror filter  $F_1$  which is transparent to short wavelength radiation  $\lambda < \lambda_1$  but reflects at long wavelengths  $\lambda > \lambda_1$  to reduce reradiation from the thermal reservoir. The input radiation is absorbed and stored in the reservoir, which has a large thermal inertia. The thermal reservoir then reradiates the energy onto a photovoltaic cell array in a narrow spectral band, which is determined by a second filter  $F_2$ , with a cutoff wavelength  $\lambda_2$  corresponding to the cutoff for the cells. Radiation at wavelengths longer than  $\lambda_2$  is reflected back into the reservoir and reabsorbed. By thus confining the output radiation to a narrow band, in a manner that has been previously discussed in connection with thermophotovoltaic converters (Ref. 1), the efficiency of the system is improved in comparison to direct solar conversion. The realization in practice of heat-mirror type filters has been investigated previously using a number of materials (Refs. 2-4).

In a design version of the thermal reservoir shown in Fig. 2, NaF at its melting point of 1265 K was selected for the storage medium in order to take advantage of the storage capacity provided by the high latent heat of 167 kcal/kg for this material. The molten material is contained in a cylindrical structure suspended by support rods. For overnight storage (24-hour electrical output) heat losses from the reservoir can be kept to about 20% of the input energy by using vacuum insulation around the NaF containment vessel and multilayer radiation shields over the passive portion of the reservoir wall. The cylindrical hole through the center of the reservoir serves to transmit the radiation to the bottom of the vessel in order that temperature throughout the reservoir can be equalized by convection. System parameters for a reservoir design aimed at minimizing the cost per kilowatt of electrical output power are as follows:

Reservoir temperature	1265 K
Collector concentration ratio	1000
Daily solar input	10 kWh/m <sup>2</sup>
Input-storage cycle	24 hours
Input filter cutoff	2 $\mu$ m
Photovoltaic cell cutoff	1.7 $\mu$ m
Overall efficiency	32%
Cost	~\$1100/kW

For a solar collector with two-axis steering, a 10 kWh/m<sup>2</sup> daily solar input is estimated (Refs. 5-8) for optimum atmospheric conditions in central U.S.

The cost of the system is dominated by the approximate \$100/m<sup>2</sup> cost of the collector. The storage cost alone, based on the usable electrical power output, is about 1/3 of the cost of battery storage. As indicated in Table 1, the cost per kilowatt is nearly constant for units with a reservoir diameter between 1 and 3.3 m.

A particularly promising cell material for use in this scheme is Pb<sub>1-x</sub>Cd<sub>x</sub>S, because its energy gap can be adjusted to an optimum value by choosing the Cd content and because large-area cells should be economically producible by inexpensive evaporation or other epitaxial techniques similar to those currently used in growing films in other lead-salt materials, such as PbTe (Ref. 9). Because of the use of a solar concentrator, a cell cost of \$200/m<sup>2</sup> – ten times the cost of Cu<sub>2</sub>S-CdS cells (Ref. 10) – would still constitute a negligible contribution to the total system cost. Since Pb<sub>1-x</sub>Cd<sub>x</sub>S is a direct-energy gap material (Ref. 11), it has a high absorption coefficient (>10<sup>4</sup> cm<sup>-1</sup>); consequently, the radiation is absorbed in a shallow layer. In properly constructed antireflection-coated cells, it should be possible to achieve a very high quantum efficiency and a low series resistance, judging from results on photovoltaic detectors (Ref. 12) in lead-salt materials. In calculating the cell efficiency a negligible series resistance, unity quantum efficiency and an ideal exponential I-V characteristic were assumed. Based on these assumptions, a power efficiency of 52% was calculated for monochromatic radiation at the response peak of room temperature operated Pb<sub>1-x</sub>Cd<sub>x</sub>S cells with a 1.7- $\mu$ m cutoff wavelength, at an incident flux of 13 kW/m<sup>2</sup>, which was estimated for the thermal reservoir system with the listed parameters.

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## Discussion

- Q: Will you describe for me the materials that you propose to use?
- A: Heat is a consideration. There are materials like indium oxide, for example, that have been used that are based on the plasma edge reflection, so that they are transparent for short wavelengths, and opaque for long wavelengths.
- Q: It is my understanding that none of these materials has a performance which is in any way adequate to do what you are proposing to do; so my concern is, how are you going to go about getting from where we are today with these conductive oxides to where you would need to be to make this practical?
- A: We find that the input filter is not too critical, because if we use a thousand-to-one concentration we come down to a window size. With such a small size that loss is not dominating. We have estimated the loss to be about 20 percent of the input due to thermal losses, reradiation, and such. Now for the second filter, you could even use the cell itself as a filter. In other words, radiation that the cell has not absorbed could go through the cell and be reflected right back with a totally reflecting mirror behind it. Now how efficient that would be, I'm not sure, but that would be an alternate scheme.
- Q: Did the \$1100 include the cost of a collector?
- A: Yes. The collector contributes about \$750 and the storage medium is not very expensive. If we estimate the storage costs per unit of electrical energy, then it comes out that it is about one third of the cost of battery storage. The cells themselves we have not really considered, because we think they are not going to be dominating. Once you use a collector, then the cell expense is not crucial.
- C: We have tried almost every aspect of this scheme in our work with thermal-photovoltaic energy conversion using thermal radiators and germanium cells. One comment I want to make is that at the operating temperature of about 1000°K, you get a very low utilization of your spectrum, which is on the order of 15 to 20 percent of the radiation energy that can actually be utilized at 1.7 micrometer absorption edge.
- A: Yes. That's about right, I think.
- Q: If you do this and you want to get good system efficiency, it means you have to utilize almost 80 to 90 percent of your nonusable energy and get it back to the source.
- A: Yes.
- C: That, I think, is the most critical problem.
- A: You are absolutely right. That constitutes all of the loss, in fact. We have assumed in the calculation that we would use this cell array; that radiation that is not absorbed by the cells could go through the cells and be reflected back. And for that reflection we assumed gold, which is about 98 percent reflecting.
- C: But there is one problem in this scheme. We have tried this in germanium. I don't know whether this will be any better in the material you have proposed. Actually in undoped germanium you get a good transparency at the absorption edge. As soon as you dope it to the levels which you need for a high power density and output voltage, you have higher absorption. And what we found is that you cannot get much beyond about 40 to 50 percent, I think, reflection from the back surface. So you have considerable losses there. On the other hand, another possibility is if you tried to put the filter right on the surface. But at the present time there are no filters available that are good enough.
- A: That could cause some argument.

Table 1. Output power and cost for three sizes of unit

Reservoir diam. $D_R$ , m	Collector area $A_C$ , $m^2$	Electrical output power $P_e$ , kW	Cost of unit, dollars	Cost per unit output power, dollars/kW
1.0	56	7.5	8,500	1140
2.5	880	117	120,000	1050
3.3	2020	270	290,000	1060

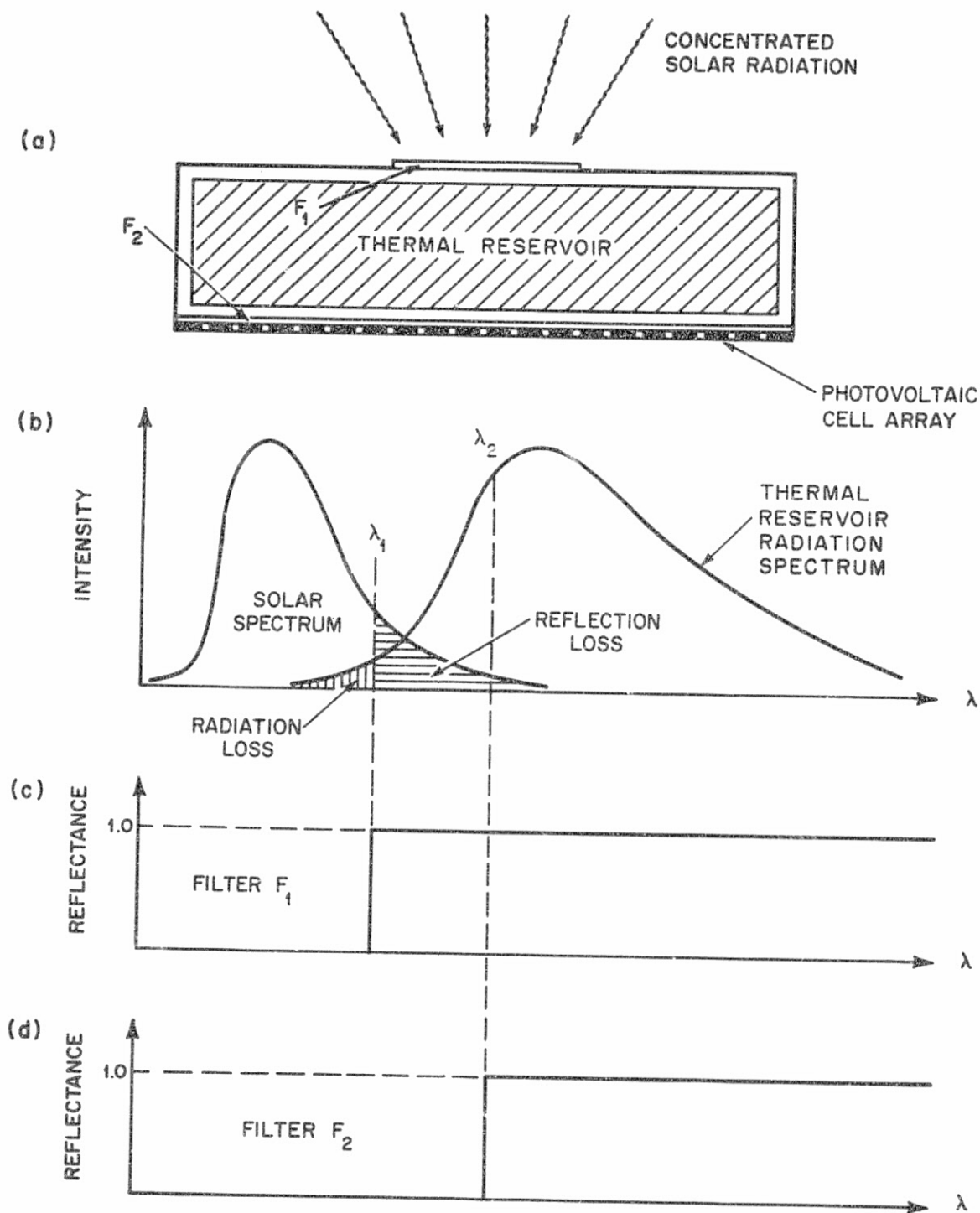


Fig. 1. (a) Solar radiation converter with idealized short-wavelength-transmitting filters  $F_1$  and  $F_2$  whose reflectivity spectra are shown in (c) and (d), respectively. The solar spectrum and the thermal reservoir spectrum are shown in (b)

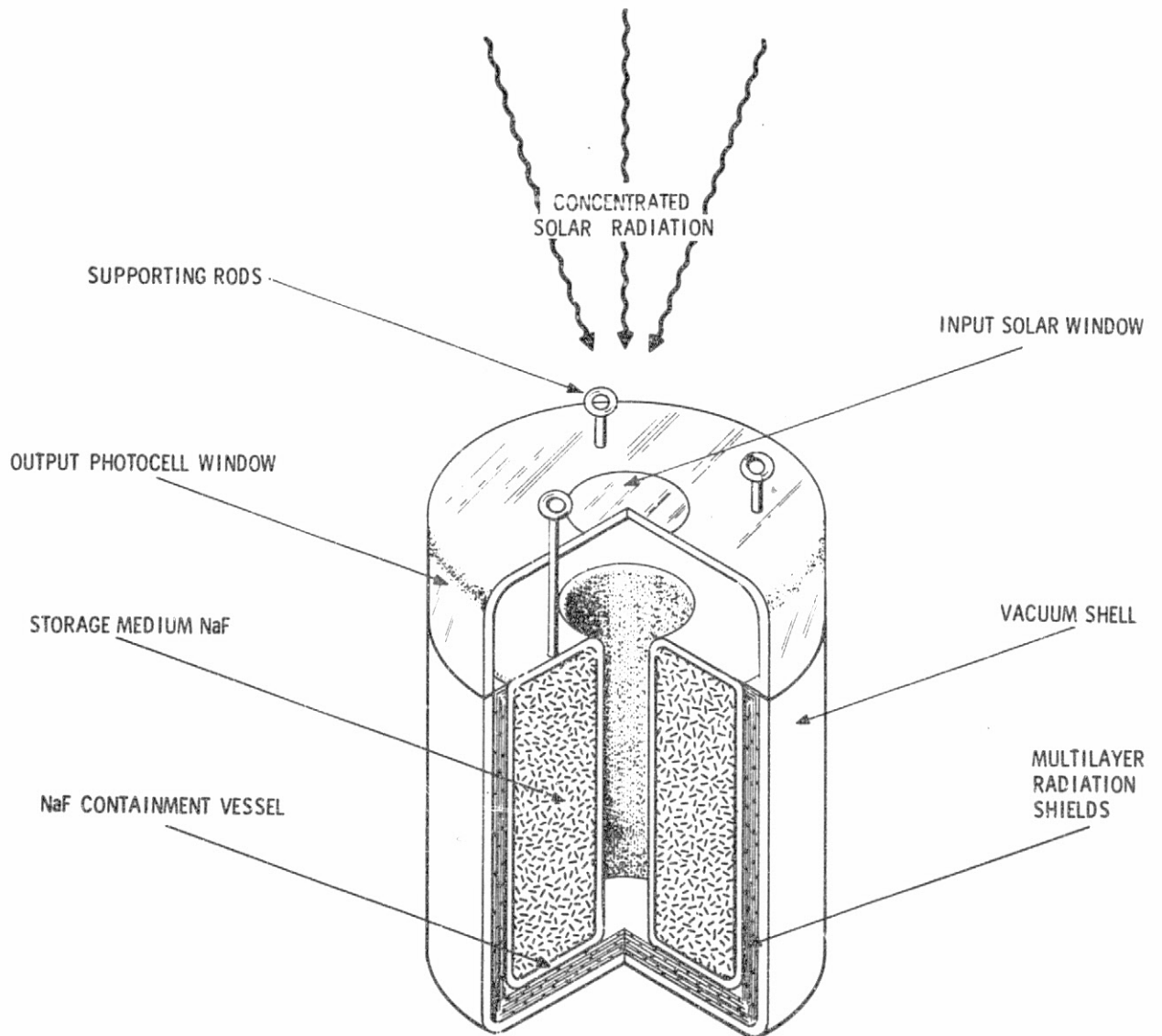


Fig. 2. Structure of High-Temperature Thermal Reservoir

## PHOTO-ELECTROLYTIC DECOMPOSITION OF WATER

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**Presentation Summary**

The short-range goal of this effort is to define the optimum configuration and to study the maximum efficiency possible in the direct conversion of solar energy to electrochemical energy. The long-range goal is to define the economic criteria for large-scale utilization of solar energy for the production of hydrogen fuel and electrical power simultaneously.

Recently, it has been demonstrated (Refs. 1, 2, and 3) that it is possible to decompose water with visible light at the interface of a semiconductor and an electrolyte. While direct photo-decomposition of the water molecule requires light with energy above 6.5 eV (in the ultraviolet, wavelength less than 190 nm), the electrolytic photo-decomposition requires only light with energy above 2 eV (wavelength in the visible, less than 600 nm). Figure 1 gives the voltage-current relationship for TiO<sub>2</sub> electrode in the dark and under illumination (oxygen evolution). Figures 2 and 3 represent the same relationship for GaP and ZnO (hydrogen and oxygen evolution, respectively). The observed photocurrent is very similar to the one obtained with a photodiode consisting of a metal-semiconductor rectifying junction and can be explained by the existence of band-bending and the consequent formation of a depletion layer. The proposed energy level diagram is shown in Fig. 4 for the interface between a p- and an n-type semiconductor and the electrolyte.

There are three general ways to increase the efficiency of the process: the first, and most obvious, is to use p- and n-type semiconductors for the two electrodes instead of a semiconductor-metal combination; the second is to use a two-photon process (one each in the two semiconducting electrodes) in order to reduce the minimum energy of light required to 1 eV (wavelength of less than 1 micron); and the last is to use the equivalent of a heterojunction, i.e., two different semiconductors for the electrodes, and thereby dividing the solar spectrum into 2 equal parts. One semiconductor with band gap of about 2 eV will absorb light with wavelength less than 600 nm. The remaining light will be transmitted to the second semiconductor electrode with a band gap of less than 1 eV, which will absorb the remaining half of the solar spectrum. This method will avoid the creation of very energetic photoelectrons with the consequent losses.

Experiments have shown that polycrystalline semiconducting thin films have less efficiency than single crystals; however, the existence of surface states in this process is beneficial since they serve as nucleation centers for the evolved gases.

Cost estimates for thin film panels on glass range from \$0.50 per square meter for ZnO to \$10.00 per square meter for TiO<sub>2</sub> and GaP. The measured quantum efficiencies for the metal-semiconductor combination are about 10%. With the improved method of two semiconductor electrodes, we hope to obtain higher efficiencies; however, even for a 10% obtained at present, some of the pertinent data are:

Electrical power produced is 0.25 volts at 2.5 A/m<sup>2</sup> or a power of 0.625 watts/m<sup>2</sup>. The hydrogen gas output is about 20 liters at STP per m<sup>2</sup> per day or the equivalent of about 20 watts/m<sup>2</sup> of chemical energy. The projected two-photon process output will be above 75 watts/m<sup>2</sup> for a 10% quantum efficiency and even higher for better electrode materials. The cost of total power (chemical plus electrical) is less than \$0.50/watt at the present, with excellent chances of going down with improved efficiency. The storage and distribution of hydrogen gas are considerably easier and cheaper in large volumes than that of electrical energy. The available electric power could be

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used to pump water from the oceans to the coastal deserts and the hydrogen gas through the pipelines to the densely populated areas in the country.

Problem areas remain in the field of electrochemical data available for non-metallic electrodes. Using dyes in the electrolyte also increases the photocurrents manyfold; however, more research is needed in this area.

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### Discussion

(Not recorded)



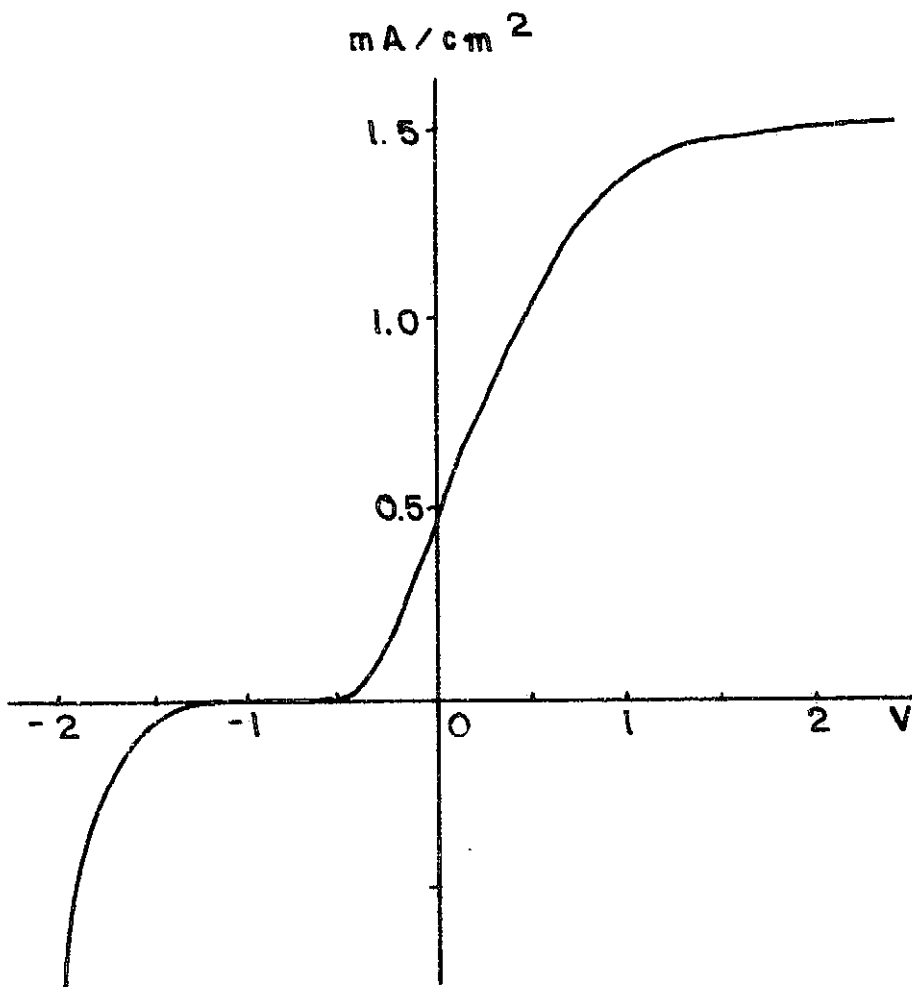


Fig. 1. Voltage-Current Relationship for n-TiO<sub>2</sub> Electrode in the Dark and Under Illumination

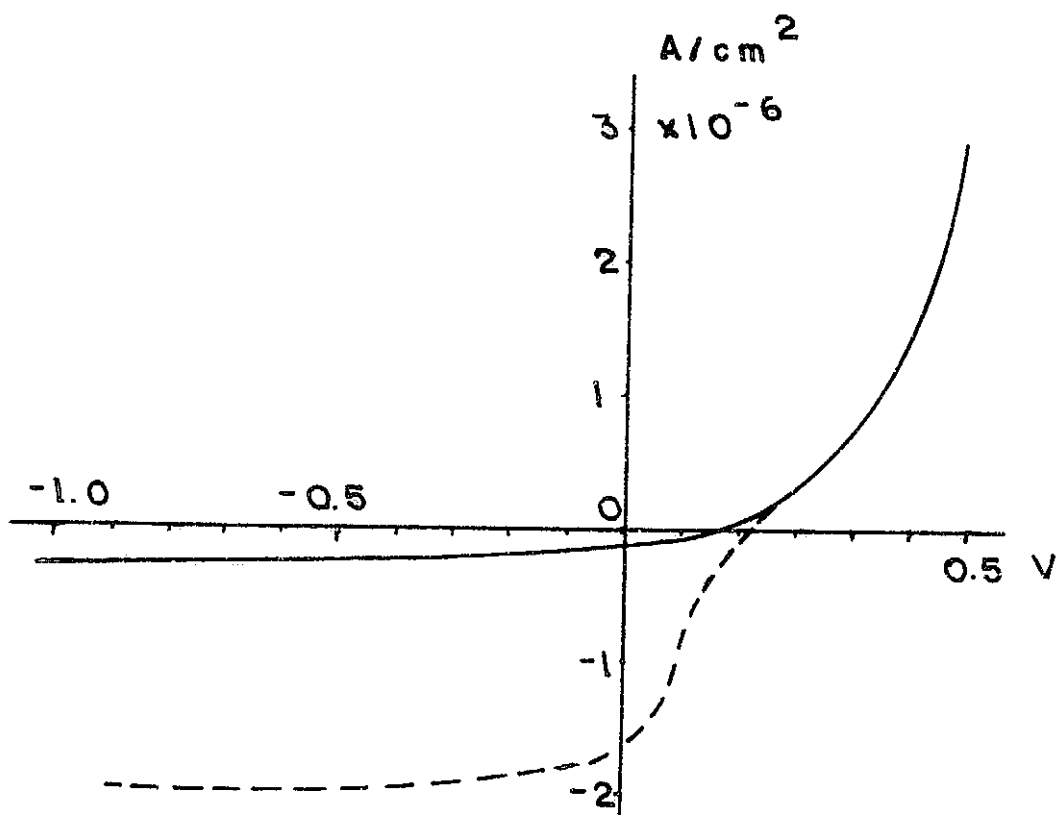


Fig. 2. Voltage-Current Relationship for p-GaP Electrode in the Dark and Under Illumination

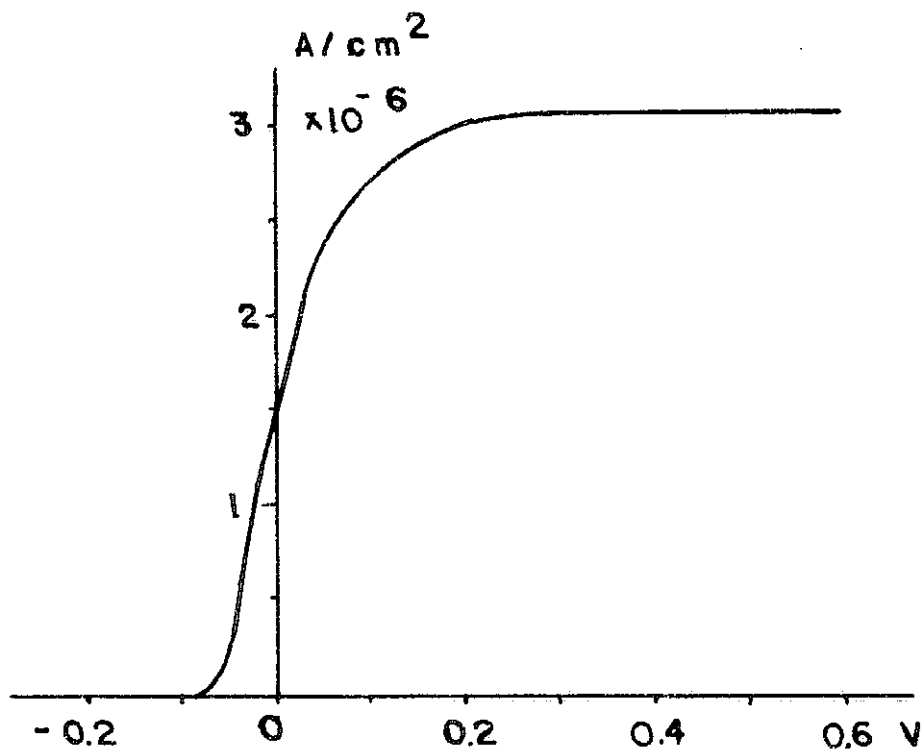


Fig. 3. Photocurrent for n-ZnO Electrode as a Function of Voltage

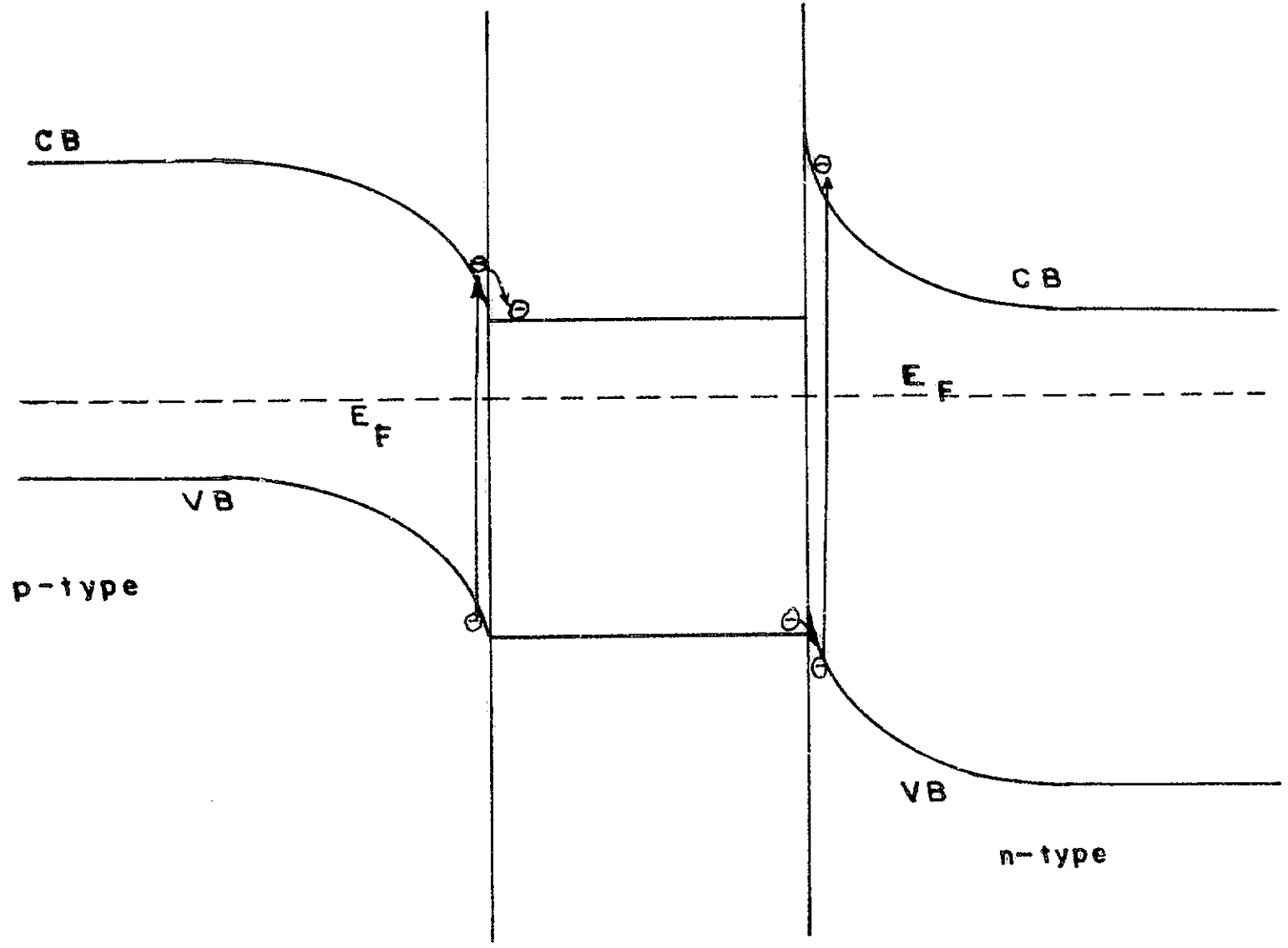


Fig. 4. Energy Diagram for the Interface Between p- and n-Type Semiconductor and Electrolyte

## ELECTROMAGNETIC WAVE ENERGY CONVERSION RESEARCH

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### Presentation Summary

#### Introduction

Present photovoltaic technology is "locked-into" the quantum approach with maximum theoretical conversion efficiencies of about 23 percent. The obvious wave approach, which also bypasses the Carnot limitation, appears to have been ignored. It has been proposed (Ref. 1) that the possibility of creating direct converters having efficiencies greater than 50 percent exists. Such converters would be based on exploiting wave properties of the incident radiation based on the invention (Ref. 2) of the Electromagnetic Wave Energy Converter (EWEC). It has been shown (Ref. 3) that the long-range market potential for such a converter on residences, commercial buildings, and centralized solar-electric plants is many *billions* of dollars.

The NSF/NASA Solar Energy Panel report (Ref. 4) recommended that EWEC research be initiated.

#### New Converter

The new converter embodiment proposed is shown in Fig. 1. In (a) the electric field  $\vec{E}$  induces currents in the pyramid or conical absorber elements (many wavelengths long) and a voltage is generated between them. It is rectified and filtered, and appears as dc power in the load. In (b) a similar arrangement exists for horizontal  $\vec{E}$  polarization; thus embodiment (b) converts either vertical or horizontal  $\vec{E}$  fields to useful power making the converter insensitive to polarization of the incident wave. A microelectronic embodiment is shown in (c).

The EWEC differs *markedly* from smooth surface quantum based conventional solar cells and is generally more like rough structures found in nature, e.g., insect antennae and eye retinas in vertebrates (Ref. 5).

#### Key Initial Research Problems

Key initial research problems are seen as:

- (1) Prior art studies in antenna and nature areas.
- (2) Metals vs dielectrics for the absorber elements.
- (3) Coupling energy out of the absorber elements.
- (4) The diode which must ultimately work in the micron wavelength range.
- (5) Microwave array performance.

The problems appear surmountable.

#### Research Goals

Research goals for the proposed Phase I research are shown in Table I.

**Research Plan**

The research plan proposed for ultimately realizing practical EWEC converters is:

- (1) *Phase I.* Theoretical-experimental research of EWEC at microwave frequencies ("scaled experiments") where optimum absorber geometries can be found and where experimental absorber elements are easy to fabricate. A small interdisciplinary team at University of Florida would conduct this research (approximately 2 years).
- (2) *Phase II.* Would take the known optimum converter geometry from Phase I and shrink it to operate at IR and solar wavelengths. Its goal would be to produce practical high efficiency converters for solar wavelengths (approximately 5-8 years additional effort).

**Background and Status**

Concept was briefly checked at microwave. Patent was filed by NASA GSFC. Technical papers were presented at several conferences. A comprehensive proposal to NSF RANN assembling 5 years part-time work on this new invention has been written and is in the review-decision process. Previous support: NASA Goddard, University of Florida, and four Florida utility companies.

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**Discussion**

(Not recorded)

Table I. Research Goals

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Broad research goals, or expected results, from the proposed Phase I research are:

- (1) To establish a better quantitative understanding (theoretical and experimental) of the EWEC invention.
  - (2) To generate the necessary quantitative theoretical base for radiant wave-electric converters of the general EWEC class so that performance and characteristics of practical converters can be reasonably predicted.
  - (3) To demonstrate a complete optimized EWEC converter operable at microwave frequencies and to determine its major measured characteristics.
  - (4) To determine at microwavelengths the extent EWEC's potential advantages of:
    - (a) High conversion efficiency
    - (b) Function separation
    - (c) Power spectrum matching capability
    - (d) Control of absorption bandwidth
    - (e) Mechanical flexibility
    - (f) Mass production capability

can, in fact, be potentially realized in the IR-solar range with practical man-made converters.
  - (5) To better understand EWEC-type structures occurring in nature, particularly insect antennae and vertebrate eyes, and to translate such insights where applicable into useful man-made EWEC-type embodiments.
  - (6) To quantitatively predict optimized EWEC performance at wavelengths shorter than microwave, i.e., IR-laser and solar ranges, in anticipation of creating a practical EWEC conversion technology in this range founded on Phase I microwave research facts.
  - (7) To lay a firm foundation for a later Phase II research effort which would make high-efficiency low-cost EWEC converter hardware practicable for the IR-solar range. Phase I research would place us in position to make a frontal assault on the key research problems in this shorter wavelength range.
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FIG. a

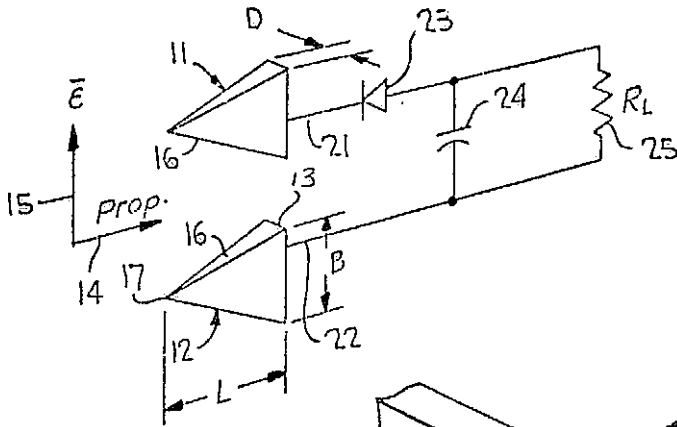


FIG. b

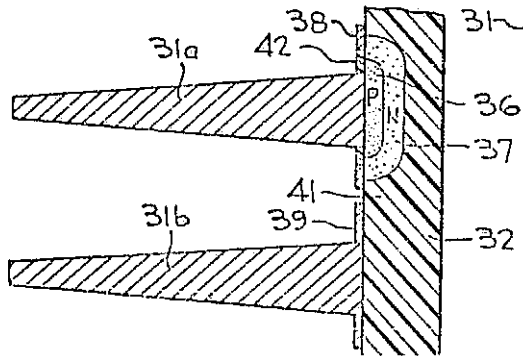
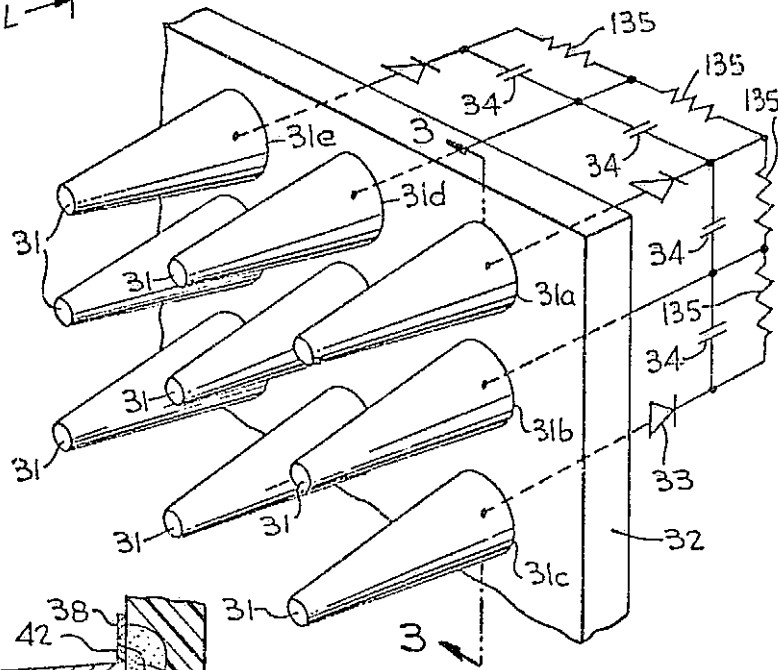


FIG. c

Fig. 1. Rough conceptual sketch of new large area electromagnetic wave energy converter absorber that might be created from the proposed research. The surface would be rough. It would utilize the wave properties of the impinging radiation. The concept is ultimately aimed at solar energy but may also have useful spinoffs for microwave and infrared ranges



## VERTICAL MULTIJUNCTION SOLAR CELLS

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### Presentation Summary

The Air Force is sponsoring a program to develop the vertical multijunction (VMJ) solar cell. The impetus for a cell of this geometry is twofold – increased operational efficiency and improved radiation tolerance. Figure 1 depicts the basic design compared to a conventional cell.

A theoretical analysis by the Air Force Aero Propulsion Laboratory determined that a vertical junction packing density of greater than 2000 junctions/cm is required to achieve both increased efficiency and radiation resistance (Ref. 1). If radiation damage is not a factor then the packing density can be dropped to 500 junctions/cm and still maintain high efficiency. These calculations are based on the step junction geometry. It was found by Heliotek that at least for low junction packing densities it was necessary to include a horizontal  $N^+$  layer across the top to maintain good voltages (Ref. 2).

Some calculations were made for the design in Fig. 1a for the concentrated sunlight application to terrestrial power generation; a packing density of 500 junctions/cm was assumed. The resultant calculations were compared with calculations for the new "shallow junction" class of cells presently under investigation. The comparison showed little advantage of the VMJ structure in output and because of possible fabrication cost factors, it is not a viable candidate for terrestrial use – at least in the configuration considered.

A brief description of the VMJ cell program being pursued by the Air Force is summarized in Fig. 2. Four design approaches are being considered with emphasis on approaches I and III shown in Fig. 2. The approach III design was first investigated by Heliotek (Ref. 2). The technology developed by Texas Instruments for the four approaches relies on: (a) orientation dependent etch, (b) narrow groove epitaxial refill, and (c) deep groove and narrow groove  $N^+$  diffusions. An approach III cell has already been fabricated to demonstrate the orientation dependent etch and deep/narrow groove diffusion; the VMJ conversion efficiency was slightly less than 6%. This cell was not optimized in that it possessed a relatively deep junction ( $\approx 1$  micron) and did not have an optimized upper contact configuration or antireflective coating; the cell size was 2 cm  $\times$  2 cm.

The VMJ cell development effort, sponsored by the Air Force was started in November 1971 with Heliotek with a subsequent follow-on program with Texas Instruments initiated in January 1972. The VMJ cell program funding is shown in the table below.

VMJ FUNDING			
FY72	FY73	FY74	FY75
\$72K	\$100K	\$175K	\$175K

To briefly summarize, it is not anticipated that the VMJ cell will compete with other types of solar cells in a terrestrial application because of cost limitation – although the VMJ efficiencies, assuming a successful program, would definitely be competitive. The main advantage of the VMJ cell concept is long-term operation in a space radiation environment.

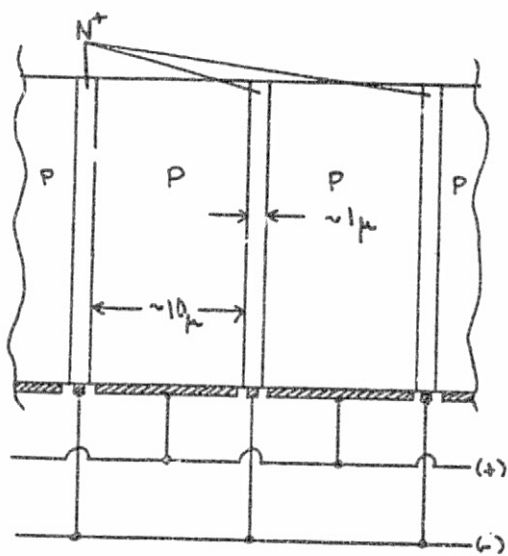
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**Discussion**

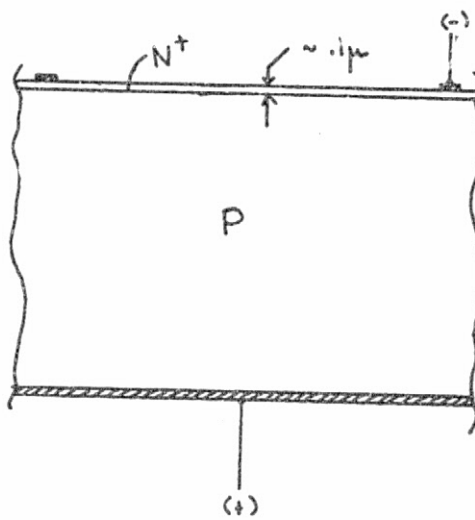
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VERTICAL MULTIJUNCTION  
SOLAR CELL



(A)

CONVENTIONAL  
SOLAR CELL



(B)

Fig. 1

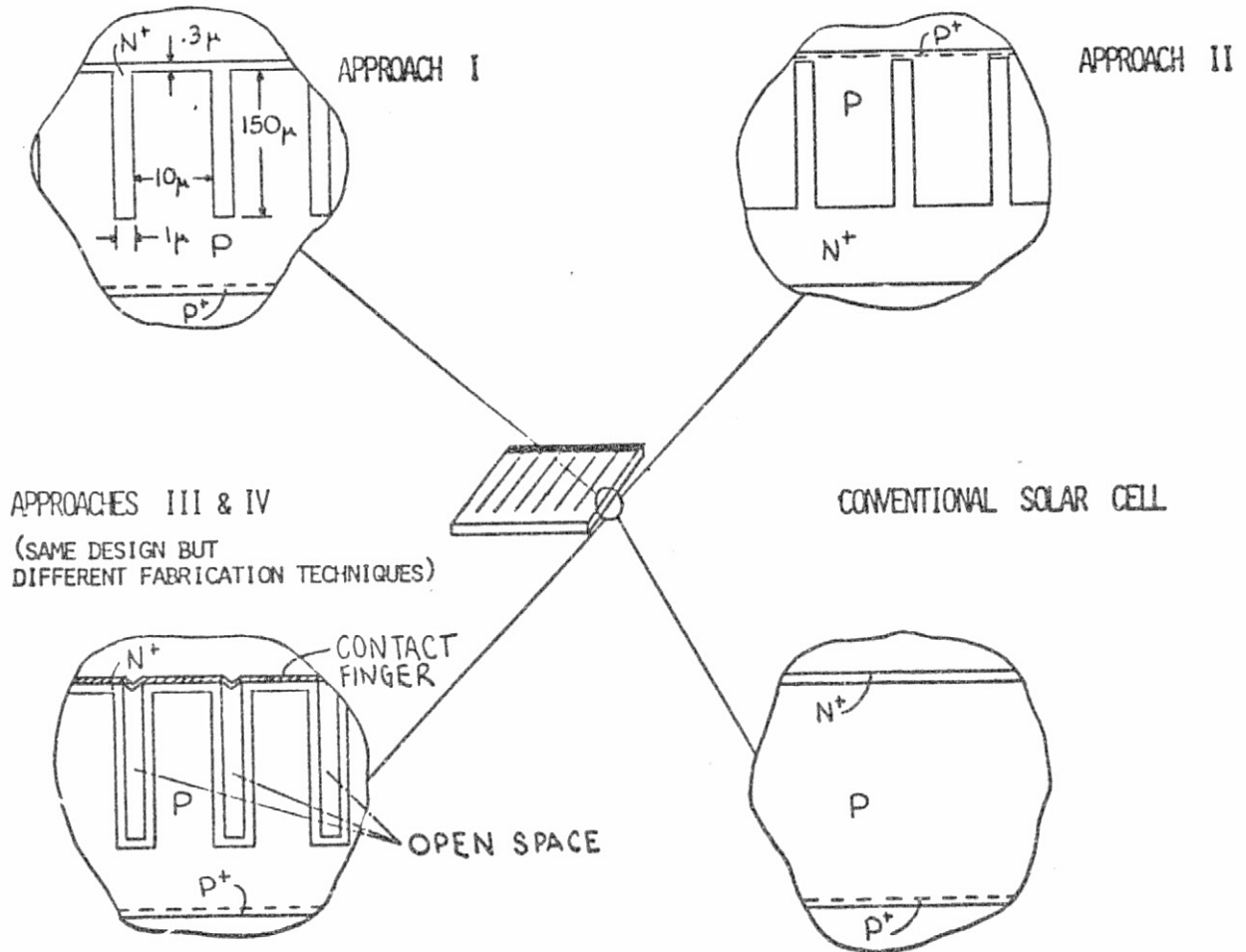


Fig. 2

**RESEARCH ON TRANSPARENT,  
ELECTRICALLY CONDUCTIVE MATERIAL\***

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**Presentation Summary**

Cadmium stannate has been found to have a large shift of the optical absorption edge towards shorter wavelengths with increasing free electron concentration (2.06 to 2.85 eV). From this observation a low effective mass is estimated indicating appreciable electron mobilities. Thin amorphous films are electrically conductive and transparent to visible light.

The fundamental electrical and optical properties of cadmium stannate suggest its use as transparent electrode in photovoltaic devices. A research program is in progress to develop cadmium stannate coatings for this application. During the first phase of the work, technology is being developed for the deposition of polycrystalline cadmium stannate films. Film crystallization has been achieved resulting in electrical conductivities approximately three times higher than in amorphous films. Further conductivity increases are expected by eliminating second phases which are still present in these samples.

Incorporation of cadmium stannate electrodes into solar cells will first be attempted with CdS/Cu<sub>2</sub>S cells. The initial objective is the replacement of the present metal backwall electrode by transparent cadmium stannate so that backwall excitation may be evaluated. This part of the program is carried out in cooperation with the Institute of Energy Conversion, University of Delaware.

**Discussion**

(Not recorded)

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\*Supported by NSF/RANN.

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