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DEVELOPMENT OF AN ALL-METAL THICK FILM COST EFFECTIVE METALLIZATION SYSTEM FOR SOLAR CELLS

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QUARTERLY REPORT NO. 2
Aug. 1980 - Oct. 1980

SEPTEMBER 1981

Contractual Acknowledgement

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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1.0 Summary

Additional quantities of pastes were procured from the subcontractor. Solar cells with junction depths varying by a factor of 3.3 were obtained from Applied Solar Energy Corporation (ASEC) with and without a deposited oxide coating. Cells were screened and fired by the two step firing process. Initial results were unsatisfactory from an adhesion and metallurgical standpoint indicating that reproducibility problems still existed.

The solar cell experiment including front contact experimentation was completed. No electrical information was obtained due to inadequate contact adhesion.

An alternative source for experimental pastes is being sought.

2.0 Introduction

The purpose of this study is to provide economical, improved thick film solar cell contacts for the high-volume production of low-cost silicon solar array modules for the LSA Project.

This work is based upon the concept of an all metal screenable electrode ink, investigated in Contract #955164. It was first found that silver powder with lead acting as a liquid sintering medium and with silver fluoride acting as an oxide scavenger, continuous adherent electrode layers result on silicon. During the final phase of the antecedent contract it was shown that base metals such as copper can likewise be sintered to provide an ohmic contact on silicon when appropriately doped. The most successful screened solar cell contacts were achieved using germanium-aluminum and silicon-aluminum eutectics as additions to the pastes for back contacts.

The objectives of the investigation are to provide all metal screenable pastes using economical base metals, suitable for application to low-to-high conductivity silicon of either conductivity type and possibly to aluminum surfaces.

3.0 Paste and Contact Experimentation

Pastes were prepared with silver fluoride obtained from several sources in order to determine the material giving optimum adhesion of fired contacts, and obtain properties reproducing earlier results[1,2].Sources included Alfa Chemical Company, Apache Chemical and Hudson Labs. A batch of S071 prepared with material from the original source of silver fluoride (Hudson Labs) did not give results distinguishable from the others.

The best paste during this contract period in color and adhesion was S071A9 prepared with Hudson Laboratories silver fluoride. Fifteen different batches of S071 were tried.

The firing process was examined, and firing experiments were carried out in three different facilities: AVX Materials Division (forming gas consisting of 90% nitrogen and 10% hydrogen) in a belt furnace, Bernd Ross Associates, two step firing process (5 minutes nitrogen followed by 8 minutes of hydrogen) in a quartz tube furnace; Applied Solar Energy Corporation, two step firing process in a quartz tube furnace.

It was found that copper pastes prepared with silver fluoride exhibited a marked change in surface color as a function of time, independent of storage conditions. The surface changed from a reddish-brown color to dark brown and in extreme cases becoming almost black in appearance. Stirring immediately restored the original color. Pastes containing all ingredients except silver fluoride did not

3.0 Cont.

exhibit a color change. While the effect of light upon silver halides is well known, this is not expected to be a factor, since pastes were kept in opaque glass containers. This phenomenon had not been observed with pastes prepared under the previous contract.

The sintering process appears to proceed in the recent pastes similarly to the previously fabricated material.

Figure 1 shows an SEM micrograph of paste S071-A18 in the dried,green (unfired) condition taken at 850X. Figure 2 shows the source ink printed on silicon and fired by the two step process at 550°C, at the same magnification. Figure 3 is the same electrode at 4250X, both micrographs indicating good sinitering action.

Optical micrography was also used as an analytical tool. Figure 4 shows an optical micrograph of S079A3 fired at 500°C (two step) at approximately 200X magnification. Figure 5 shows S071A10 fired at 550°C at the same magnification. Despite the higher temperature S071A10 appears to be more fine-grained. This may be due to the absence of the eutectic phase (Aluminum-Silicon) which lowers the system melting point of S079A3. Figure 6 shows the edge of a screened print of 71A9 fired at 550°C (two step) same magnification, and Figure 7 is similarly taken at the center of the electrode. Figure 8 shows a print under the same conditions except fired at a slightly higher temperature 575°C. Since the magnifications are identical on all these micrographs,

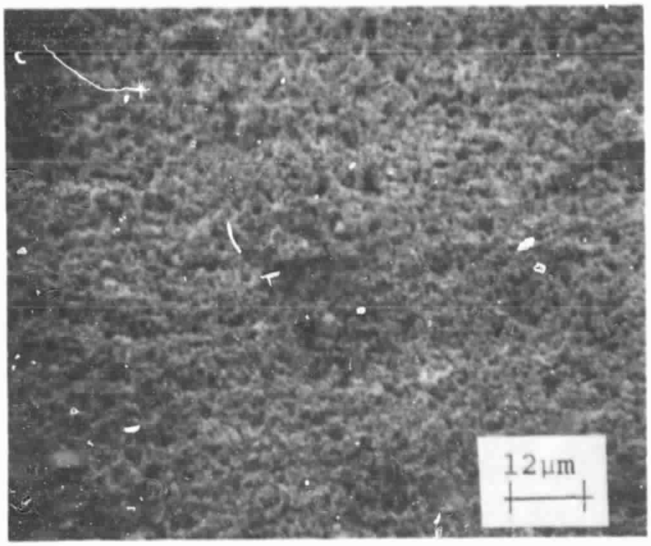

Fig. 1 SEM Micrograph of an unfired S071-A18 print, dried at 900°C, 850X.

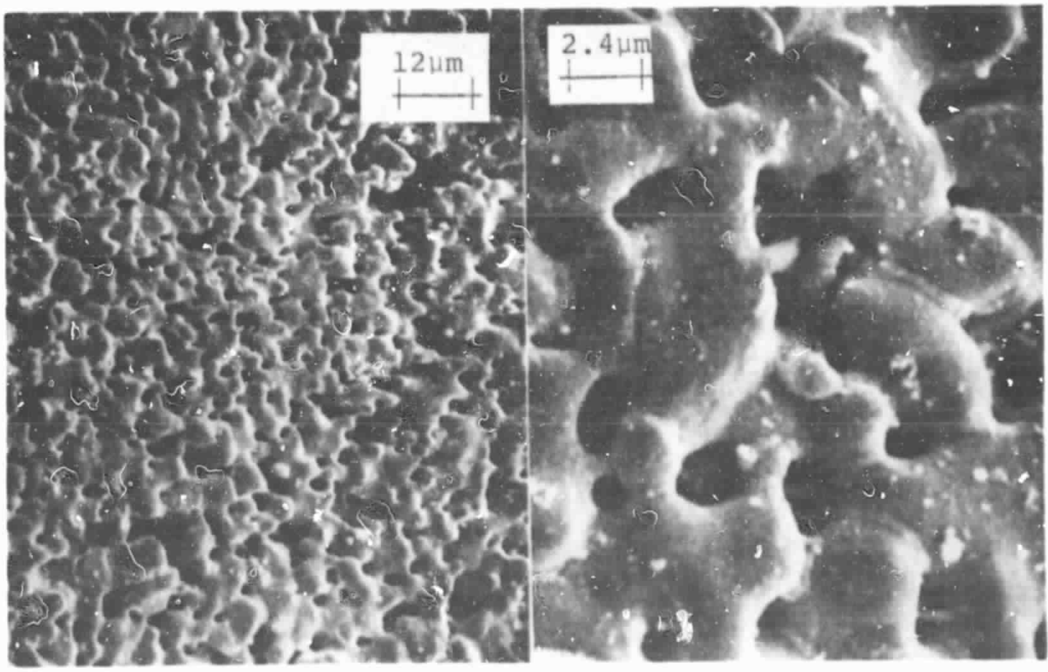

Fig. 2 Mag. 850X

Fig. 3 Mag. 4250

SEM Micrograph of S071 print fired at 550°C by the nitrogen-hydrogen two step process.

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OF POOR QUALITY

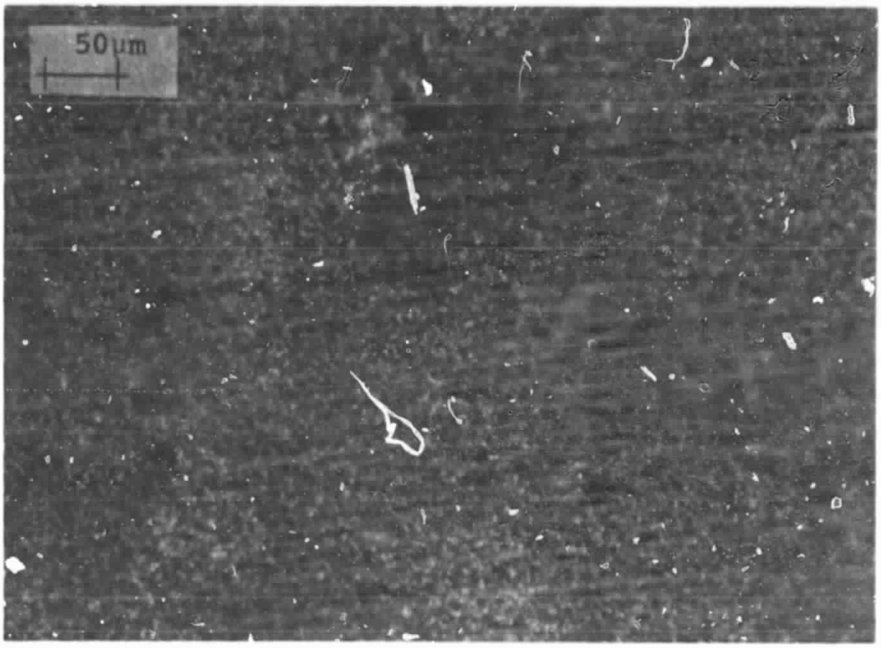

Fig. 4 Optical micrograph of S079A3 print (with eutectic dopant), fired at 500°C (two step) at 200X.

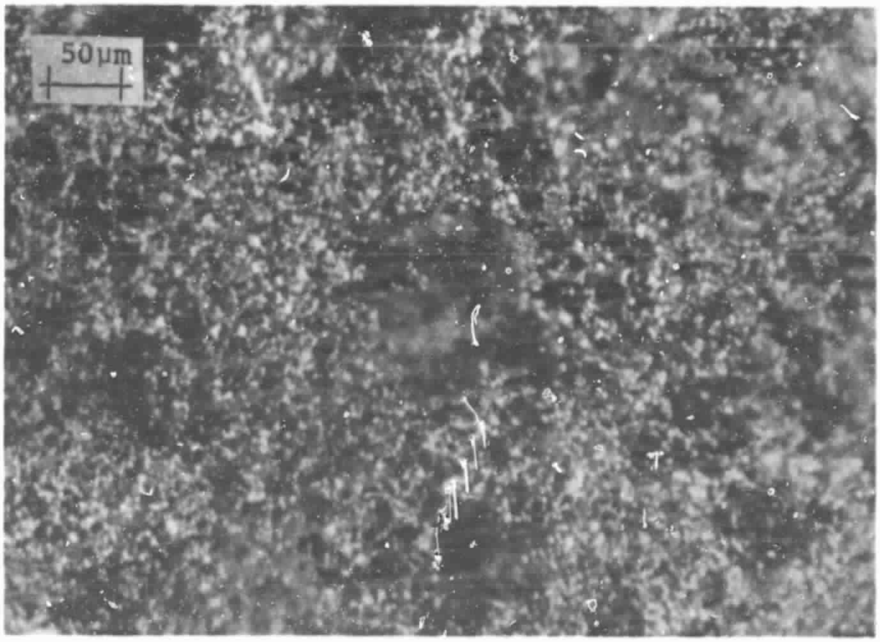

Fig. 5 Optical micrograph of S071A10 print (undoped) fired at 550°C (two step) at 200X.

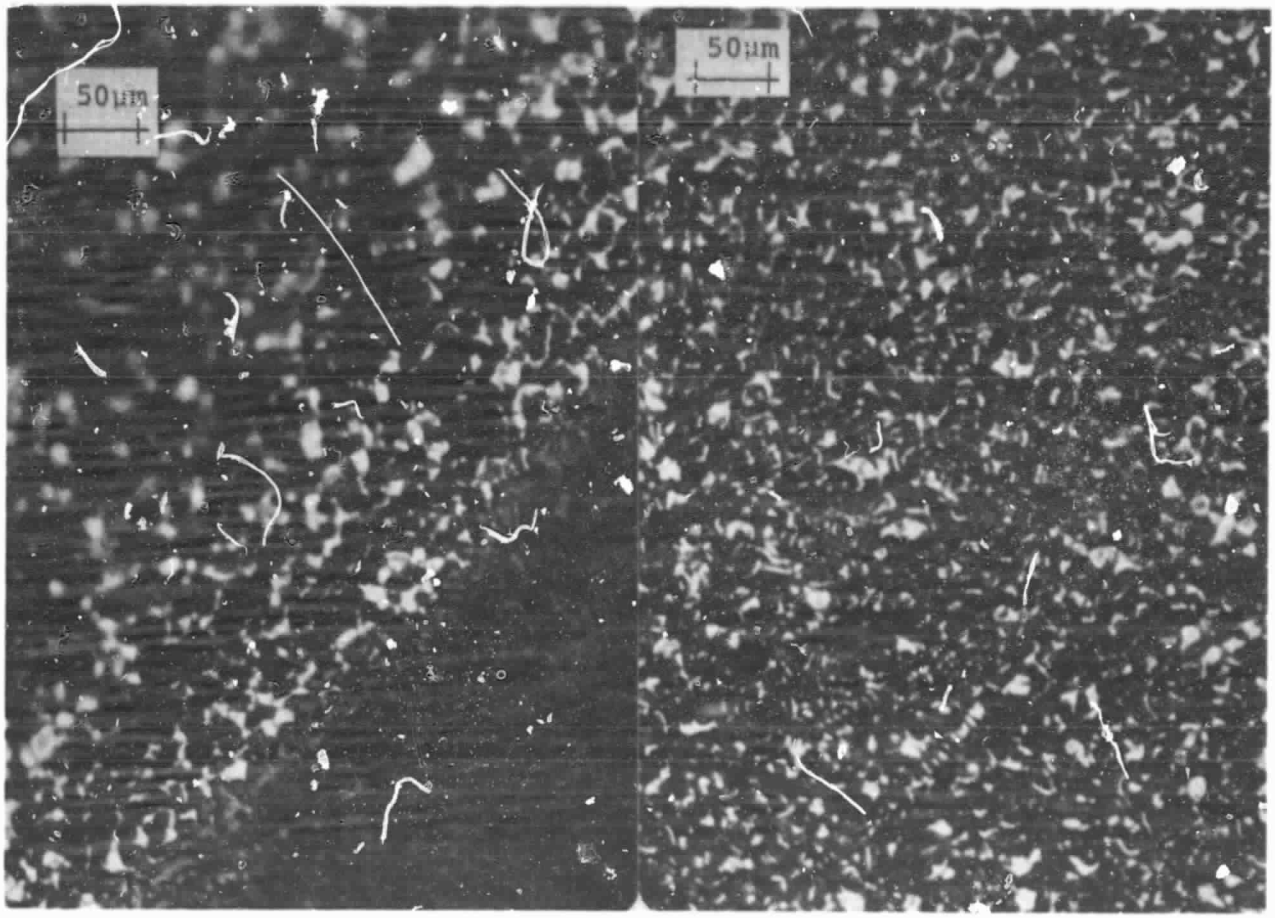

Fig. 6 Edge of print   Fig. 7 Center of print
Optical micrograph of S071A9 fired at 550°C. Magnification 200X

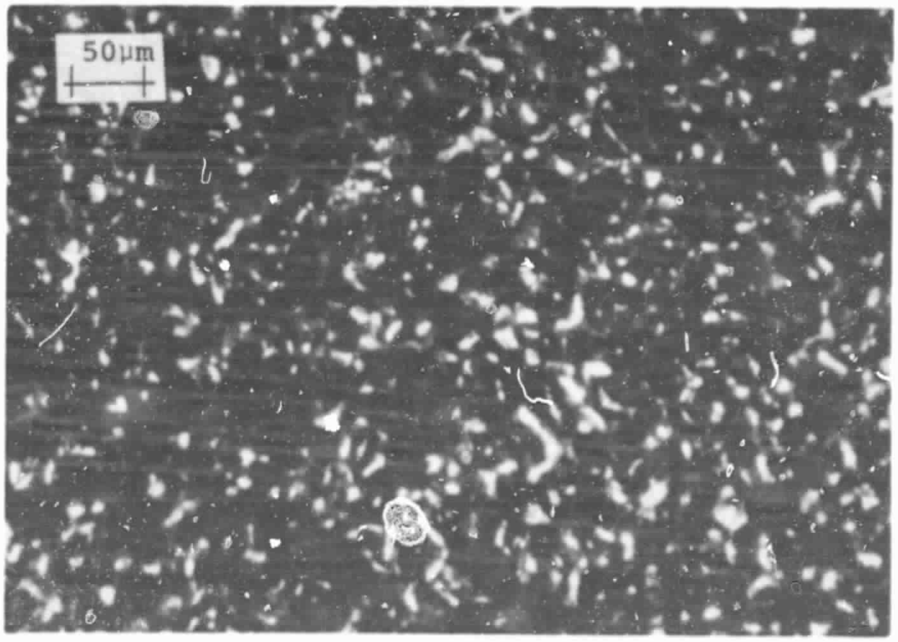

Fig. 8
Optical micrograph of S071A9 fired at 575°C.
Magnification 200X.

3.0 Cont.

it is obvious that the 25°C temperature differential in the isochronal sintering experiment leads to significantly greater grain growth.

Larger quantities of pastes were ordered from the subcontractor in order to allow beginning of small pilot line quantities of solar cells, for back contact reliability studies as well as front contact experimentation.

S071 which may be considered a master paste containing 5wt% silver fluoride, 5wt% lead, and the remainder 90wt% copper was ordered in the amount of 500 grams. Either n type or p type silicon adapted pastes can be provided from S071 by addition of the appropriate doping powders and remilling the resulting mixture.

S079, intended for contacting p type silicon and consisting of 5wt% silver fluoride, 5wt% lead, and 5wt% aluminum-silicon eutectic powder with 85wt% copper, was ordered in quantity of 100 grams.

S080, also intended for contacting p type silicon and consisting of 5wt% silver fluoride, 5wt% lead, and 5wt% aluminum-germanium eutectic, with the remainder (85wt%) copper, was ordered in quantity of 100 grams.

S093, intended for contacting n type silicon and consisting of 5wt% silver fluoride, 5wt% lead, and 5wt% antimony-silicon eutectic with the remaining 85wt% copper, was ordered in quantity of 100 grams. S071 can potentially be used for contacting

3.0 Cont.

either n or p type silicon surfaces without dopant additives, particularly if the surface concentration of impurities in the silicon, or the conductivity, is relatively high. This aspect will be examined in more detail in the next section 4.0).

4.0 Front Contact Considerations

The front contact of modern solar cells is applied to nearly degenerate n type semiconductor surfaces with impurity concentrations from $10^{19} \frac{\text{atoms}}{\text{cm}^3}$ to $10^{21} \frac{\text{atoms}}{\text{cm}^3}$ with phosphorous being the donor conventionally in use. Due to the high surface concentration and resulting high conductivity in accordance with

$$(1) \qquad \sigma = nq\mu \ (\Omega\text{cm})^{-1}$$

where
σ = conductivity $(\Omega\text{cm})^{-1}$
n carrier concentration, cm^{-3}
q electronic charge, coulombs
μ mobility, $\frac{\text{cm}^2}{\text{Vsec}}$

it is relatively simple to provide a good ohmic contact to the front surface of solar cells. This results from the fact that the electron tunneling probability is a function of the carrier concentration on both sides of the interface. When a metal coats the surface of a semiconductor, the depletion width within the semiconductor shrinks as a function of carrier concentration, thereby enhancing the tunneling probability. An enhanced tunneling probability provides for ready carrier flow through the barrier constituted by the contact potential between contact metal and semiconductor surface.

The equations governing the physics of metal semiconductor contacts[3] are given below..

The depletion width, W, can be calculated from

$$(2) \qquad W = \sqrt{\frac{2\epsilon_s}{qN_{D,A}} \left(V_R + V_D - \frac{kT}{q}\right)} \quad \text{cm}$$

4.0 Cont.

where e_s ≡ permittivity of the semiconductor, F/cm

q ≡ electronic charge, Coulomb

$N_{D,A}$ ≡ donor, respectively acceptor concentration, cm^{-3}

V_R ≡ applied bias voltage, $V_R = 0$

(3) V_D ≡ $\phi_B - \phi_n$ ≡ contact potential = 0.767eV

ϕ_B ≡ metal - semiconductor barrier = 0.80eV

(4) ϕ_n ≡ $E_c - E_F = 9.9326$eV

E_c ≡ Conduction band edge potential, eV

E_F ≡ Fermi energy, eV

k ≡ Boltzmann constant J/^{O}K

T ≡ Absolute Temperature ^{O}K

The barrier height of copper is 0.80eV, $N_D \equiv 1.10^{20}\ cm^{-3}$ (Ref.4), $e_s = 1057.10^{-12}$ F/cm, $q = 1.602.10^{-19}$ Coulomb. This yields a depletion width of

$$W = 3.13 \cdot 10^{-7} \text{ cm or } 31.3 Å$$

in the silicon.

The maximum field ε_m is given by

(5) $$\varepsilon_m = \sqrt{\frac{2qN_{D,A}}{s} \left(V_R + V_D - \frac{kT}{q}\right)} \qquad V/cm$$

and for our case yields

$$\varepsilon_m = 4.74.10^6 \ V/cm$$

The contact resistance can be calculated from the tunneling conductance

(6) $$R_c = G_o^{-1} = 10^4 \left(\frac{h}{q}\right)^2 \frac{W}{\sqrt{2qm^* \phi_o}} \exp a \sqrt{\phi_o} \quad \Omega cm^2$$

(7) where $a \equiv \frac{4\pi W}{h} \sqrt{2qm^*}$

h ≡ Planck's constant

m^* ≡ 0.1905 m the effective electronic mass in the <100> direction

ϕ_o ≡ $Eg - \phi_B = 0.42$eV

E_g ≡ Energy gap of silicon = 1.11eV

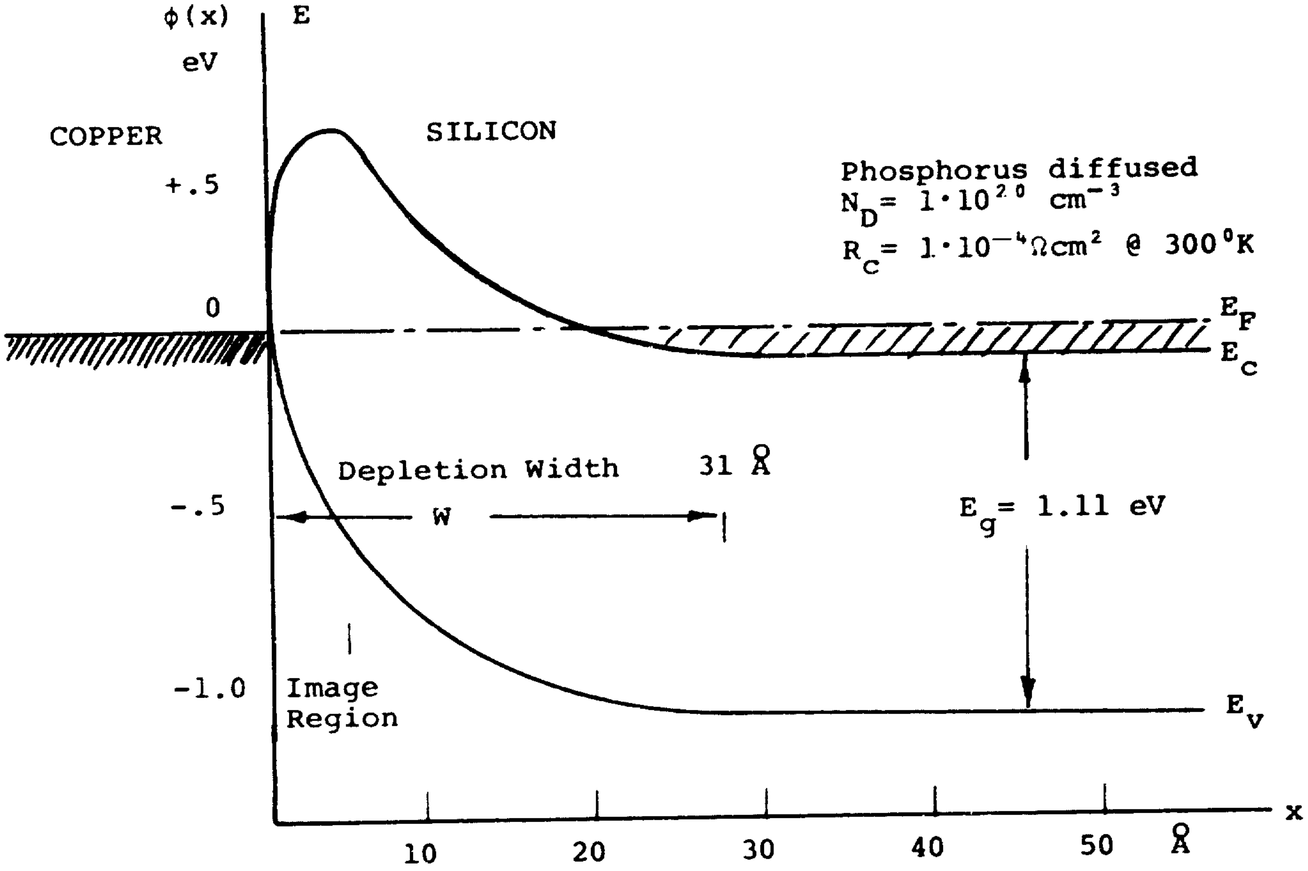

Figure 9. Energy level diagram of copper contact to front of silicon solar cell.

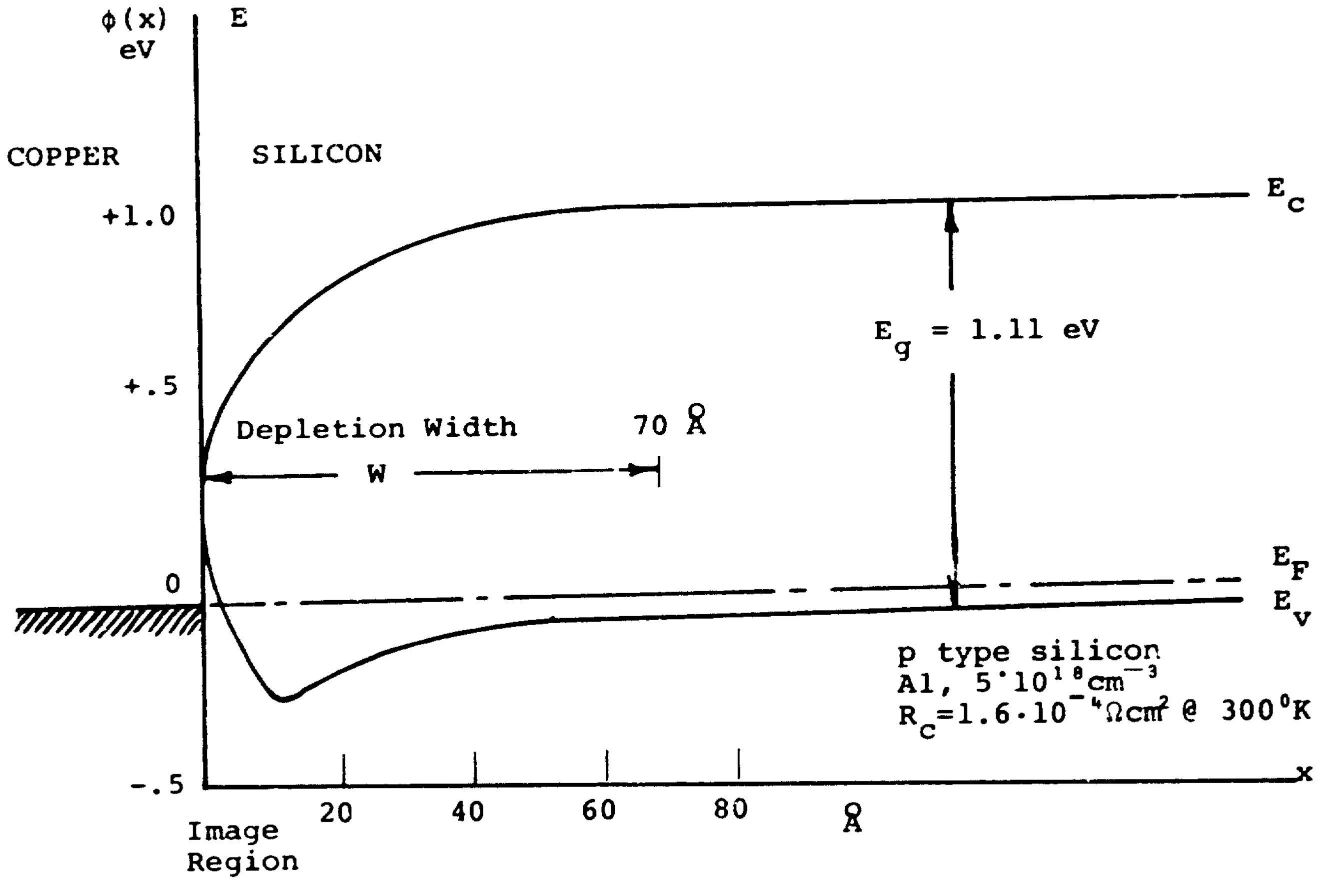

Figure 10. Energy level diagram of aluminum alloy regrowth back contact to solar cell.

4.0 Cont.

The calculated contact resistance is

$$R_C = 1 \cdot 10^{-4}\ \Omega cm^2$$

The energy band relationships for a copper contact on a silicon front surface doped with 1.10^{20} phosphorous atoms are shown in Figure 9 using the values calculated above. For the sake of completeness an energy band diagram is included in Figure 10 depicting the back contact relationships for a BSF cell, or a copper contact containing eutectic aluminum-silicon additive. For the case of aluminum-germanium (S080) a hetero epitaxial situation exit, leading to band gap narrowing on the semiconductor side of the contact (E_g (germanium) = 0.65eV.)

When the semiconductor surface has a higher resistivity, it may be necessary to make special provisions in applying the ohmic contact by utilizing a technique to dope the surface of the semiconductor under the electrode metal. When firing temperatures are sufficiently high (∿800°C) this may be done by including an elemental donor impurity in the metal and allowing it to diffuse into the semiconductor during the firing step, by solid state diffusion. Since only the surface needs to be doped, the donor atom must become a substitutional impurity in the silicon lattice within a few lattice spaces of the surface. A brief firing period will usually suffice.

At very low temperatures ($\lesssim$600°C) it may be difficult to obtain a sufficient surface concentration of dopant atoms by

4.0 Cont.

diffusion and therefore a different technique is employed. A eutectic alloy of dopant and semiconductor material is made a part of the electrode paste with the object of getting some of the eutectic to bridge semiconductor and metal. During the firing step the eutectic melts, dissolving more silicon. As the temperature is lowered again the dissolved silicon precipitates on the surface, retaining donor solid solubility concentrations, and thereby facilitating ohmic contact. Since the solid solubility of some elements in silicon is small, the use of this method is beneficial only when the front surface donor concentration is less than the donor solid solubility.

Two pastes were prepared for the front contact experiment. S071 is an undoped copper paste, which should provide the desired contact on phosphorous diffused solar cells, by virtue of the above arguments. A paste was also prepared to address the second possibility, providing an epitaxial crystalline layer, doped with antimony. This paste was fabricated by producing an eutectic alloy of antimony-germanium, reducing the resulting ingot to powder, and adding the material to the paste (5wt%).

Since antimony oxidizes readily we tried to determine the effect of our two step firing process upon doping efficiency. Copper metal was oxidized in air. It was then placed in the furnace into a hydrogen ambient. It was found that copper oxide can be reduced in hydrogen at temperatures as low as 200°C.

4.0 Cont.

By contrast it is well known that silicon oxide or aluminum oxide cannot be reduced in hydrogen at temperatures below the melting point of silicon (1420°C). The heats of formation for some of the pertinent elements are given in Table 1.

TABLE 1

Heats of Formation of Certain Oxides[5]

Reaction	Applicable Temperature	Heat of Formation
$2Sb + 3/2O_2 = Sb_2O_3$	298.16°K - 842°K	-169.450 Kcal/mol
$Bi + 1/2O_2 = BiO$	298.16°K - 544°K	- 50.450 "
$Si + O_2 = SiO_2$	298.16°K - 848°K	-210.07 "
$2Al + 1/2O_2 = Al_2O_3$	298.16°K - 931.7°K	-404.080 "
$Cu + 1/2O_2 = CuO$	298.16°K - 1357°K	- 37.710 "
$Pb + 1/2O_2 = PbO$	298.16°K - 600.5°K	- 52.800 "
$2In + 3/2O_2 = In_2O_3$	298.16°K - 429.6°K	-220.4 "
$Ni + 1/2O_2 = NiO$	298.16°K - 633°K	- 57.64 "

5.0 Solar Cell Experiment

Contacts were screened on 2¼" diameter solar cell blanks and fired at Applied Solar Energy Corporation (ASEC). None of the contacts had sufficiently good adhesion to allow electrical tests to be made. In most cases, the electrodes lifted during the sintering step, separating from the substrate wafer as a continuous sheet. This would indicate that the initial step is flawed, while sintering appears to proceed normally. Cells furnished by ASEC consisted of 5-6 each with 20 minute diffusion at 875°C estimated junction depth (assuming complementary error function solution to Fick's laws of diffusion) $3 \cdot 10^{-5}$cm. Similar quantities were furnished diffused for

40 minutes, estimated junction depth $4 \cdot 10^{-5}$cm
80 minutes, estimated junction depth $6 \cdot 10^{-5}$cm
& 200 minutes, estimated junction depth $7 \cdot 10^{-5}$cm

all at 857°C. The diffused layers had sheet resistivities of 27, 21, 16 and $11^{\Omega}/\square$ respectively.

A chemically deposited silicon oxide coating of a thickness of approximately 5,000Å was present on approximately half of the cells.

The rationale underlying the experimentation was as follows: earlier experiments [1,2] demonstrated the etching action of silver fluoride upon a thick thermal oxide layer on silicon. It is therefore believed that paste patterns screened upon the oxide layer will remove reasonable thicknesses of oxide, directly under the areas covered by paste. This will allow the AR coating to be applied during, or immediately after the phosphorus diffusion. The contacts can then be applied subsequently, without the need of masking and alignment problems, thereby resulting in simplified processing and consequent cost savings. Further, the use of the AR coating is expected to inhibit potential dissolution of the silicon surface by the etching action of the nascent fluorine.

Details of the experiment are described in the appendix.

6.0 Conclusions and Problems

Despite a large number of trials, multiple sources of chemicals and different firing sites, earlier results with copper paste have not been reproduced. Analysis, to date, of raw materials, pastes and fired electrode structures has not yielded information capable of explaining the differences. The rapid turnover of technical personnel at the subcontractor's facility was considered a factor in this problem.

The solar cell experiment similarly yielded contacts characterized by poor adhesion so that no electrical measurements could be performed.

Theoretical considerations indicate that a neutral (undoped) screened contact can be used on the front surface of phosphorus diffused solar cells without degrading performance.

The PVSEC (Oct. 1980) was attended and a paper was presented, and several German research organizations were visited. Details of the information exchange and its effect upon our activity will be treated in a future report.

7.0 Plans and Recommendations

Solar cells, electrodes and pastes will be further analyzed to determine the difference between present pastes and those made previously.

Firing conditions will be varied, including ambient gases, furnace temperatures and times, furnace furniture and others.

Alternate sources of paste manufacture, experimentation and analysis will be sought and investigated, in order to gain more complete control over material and processes by contract scientific personnel.

Since silver fluoride is the most problematic component of the present base metal paste, and since it was one of three silicon oxide scavenging agents during the initial contract #955164, it is of interest to examine some of the other materials in combination with base metal pastes. The first such material is fluorocarbon powder.

This constitutes a deviation from the original program plan.

8.0 Appendix, Solar Cell Experiment.

Appendix 1 Back contact experiment

Appendix 2 Front contact experiment
Front and back contact experiment

Appendix 1

Back Contacts Screened, Experiment I

Material: 20 cells (2 ¼" OD) with evaporated front contact

1. Printing:
    Print 6 each with S071 (Back's only)
    Print 6 each with S079 (Back's only)
    Print 6 each with S080 (Back's only)

    Total 18

2. Firing:
    Set furnace at 500°C
    Set N_2 flow
    Insert boat with cells 8" into furnace tube
        wait 5 minutes
    Slowly push to furnace center (2 minutes)
        wait 5 minutes
    Turn on H_2 flow
        wait 5 minutes
    Remove boat by slow withdrawal to position 8" from tube exit
        slow cool 5 minutes (minimum)

3. Sample Distribution
    Two each from above print groups (1) plus control (unprinted back)
        set furnace at 550°C

Repeat above(2)

2 each from above print groups

set furnace at 600°C

Repeat above 2

2 each from above print groups(1)plus control with imprinted back

4. Control — Evaporate normal Ti-Ag contact on 2 controls after thermal cycle.

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Appendix 2

Front Screened, Experiment I

Materials: 10 cells (2 ¼ " OD) with evaporated back contact (Ti-Pd-Ag)

1. Printing: Print 3 each with SO71 (Front only)
   Print 6 each with SO93 (Front only)

   Total 9

2. Firing: Set Temperature 500°C
   Cool N_2 5 minutes
   Insert 2 minutes
   Hot N_2 5 minutes
   Hot H_2 5 minutes
   Slow withdrawal 3 minutes
   Repeat 555 °C
   Repeat 600°C

3. Sample distribution
   One each print group

Front Experiment II

Utilizes previously furnished wafers with different diffusion times and SiO_2 deposited as well as bare front surfaces.

1.	200 minute	2 oxidized	3 bare
Front:	Print one(1) each SO71, SO93 (Retain 1 bare for control)		
Back;	Print all SO80		
2.	20 minute	2 oxidized	2 bare
Front:	Print one(1)each SO71, SO93		
Back:	All SO80		
3.	80 minute	1 oxidized	1 bare
Front:	Print with SO71		
Back:	SO80		
4.	40 minute	1 oxidized	1 bare
Front	Print with SO71		
Back	SO80		

Firing; as before (above) at 555°C only

Control; Put through firing cycle with parts (1) then apply normal Ti-Ag contact.

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10.0 Reference

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5. Handbook of Chemistry and Physics 56th Ed. 1975-76 p.45-50, CRC Press, Cleveland, OH.

10.0 PROGRESS ON PROGRAM PLAN

PROGRAM	▽ Start	MONTHS AFTER AWARD												
ACTIVITY	Δ Complete	1	2	3	4	5	6	7	8	9	10	11	12	13
Cu Metallization (A)		▽	—	—	Δ —	—	—							
Metallization (B)				▽			Δ							
Metallization (C)						▽				Δ				
Metallization (D)								▽				Δ		
Analysis and Test		▽	—	—	—	—	—						Δ	
Cell Delivery												.		
Cost Analysis - SAMICS												.		
Reports - Monthly			x	x		x	x		.	.		.		
- Quarterly					x			x			.			
- Final													.	
Review Meetings					x		x			.			.	.
Project Integration Meetings		x					x				.			
Project Workshops					As Specified By JPL									

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