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High Efficiency Thin-Film GaAs Solar Cells

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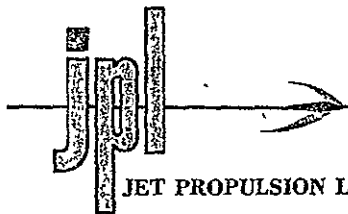
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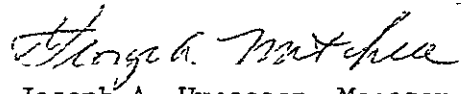
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High Efficiency Thin-Film GaAs Solar Cells

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September 1977

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Space Administration

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DEFINITION OF ABBREVIATIONS

AMOS - Antireflection-Coated Metal Oxide-Semiconductor

XPS - X-ray Photoelectron Spectroscopy

CVD - Chemical Vapor Deposition

AR - Antireflection

CMRR - Common Mode Rejection Ratio

LIA - Lock-in Amplifier

PAR - Princeton Applied Research

LED - Light Emitting Diode

SAF - Surface Analysis Facility

EBIC - Electron Beam Induced Current

EDAX - Energy Dispersive Analysis X-Ray

ABSTRACT

A solar-cell research task was begun in January, 1976 with the following objectives: (1) to investigate the feasibility of growing large-grain polycrystalline GaAs by chemical vapor deposition on recrystallized Ge films, (2) to fabricate AMOS (Antireflection-Coated Metal-Oxide-Semiconductor) solar cells on the films, and (3) to investigate the physics and chemistry of AMOS solar cells on single crystal GaAs.

Results from the single crystal studies have shown that, of the various oxidation techniques investigated for producing oxide layers, exposure of GaAs to water vapor-saturated oxygen at room temperature gives the largest improvement in open-circuit voltage (V_{OC}) to date. Equally important for high V_{OC} is the manner of surface cleaning and handling prior to oxidation. The enhancement of V_{OC} appears to be linearly dependent on exposure time to the oxygen, and hence, to oxide thickness, or more accurately, to oxide coverage. Maximum values obtained for V_{OC} at 28°C were about 800 mV with a cell efficiency of 16% at AM1 sunlight intensity. The reverse saturation current density was as low as 4×10^{-14} ampere/cm² with corresponding fill factors of up to 83%. Other oxidation processes explored included the use of ozone, glow discharges in O₂, and aqueous and non-aqueous anodization.

XPS (X-ray Photoelectron Spectroscopy) results show that the most effective oxide, that grown in water vapor-saturated O₂, has an arsenic oxide to gallium oxide ratio of 0.85-the lowest ratio for any oxide investigated. The arsenic oxide was predominately As₂O₃, as compared to ozone-generated oxides, for example, which had predominantly As⁺⁵ (possibly in the form GaAsO₄). Increased solar cell efficiency was found to correlate with oxides which are composed primarily of As₂O₃ and Ga₂O₃, with little GaAsO₄.

Attempts to correlate the oxide chemistry and photovoltaic parameters with information on localized states at the oxide-GaAs interface were made on a subcontract to Pennsylvania State University. Specific information on interface state densities, energy distributions, or capture cross-sections has not been generated to date. Rather, considerable effort has gone into the exploration of capacitance-conductance techniques which may be adaptable to the relatively high conductance GaAs oxide films. Details of a lock-in amplifier impedance measuring system specifically designed for the system under investigation are given.

Earlier problems with open-circuit voltage losses of 100-150 mV upon electron-beam deposition of Ta₂O₅ antireflection coatings have been solved with the use of either laser flash evaporation which prevents dissociation and minimizes sample heating, or resistance-heated boat evaporation of Sb₂O₃, which evaporates at a lower temperature than most dielectrics.

Preliminary heat-treatment experiments showed that, as expected, gold-GaAs Schottky barriers are not stable above 100°C due to Ga out-diffusion and Au diffusion into the bulk. The effect was to lower the barrier height enough to cause up to 100 mV loss in V_{OC} . Metals

such as silver or copper are expected to tolerate higher temperatures, and yet give equally good initial cell efficiencies.

Schottky barrier solar cells were fabricated on sliced wafers of bulk polycrystalline GaAs to provide intermediate results of the effect of grain boundaries, if any, on the cell properties. Both scanning electron microscopy and short-circuit current measurements showed that there were negligible effects when a GaAs epitaxial layer is grown on the wafer, with intra-grain properties comparable to single crystal epitaxial layers. This is not unexpected for the grain sizes of 100 μ m or more observed in the samples.

However, values of V_{oc} for cells fabricated on such samples using ozone or oxygen glow discharge oxidations were about 15% lower than those obtained on single crystals, although values on unoxidized surfaces (baseline) were comparable for both types of GaAs. At this time, the preferred oxidation technique using water vapor-saturated O_2 has not been investigated for polycrystalline GaAs wafers.

In addition to the importance of having a solar cell structure and fabrication technique that is low cost, amenable to automated production, and adaptable to thin-film polycrystalline GaAs films, equal importance must be given to the development of thin-film GaAs. Using tungsten substrates, we have demonstrated both the advantage of using recrystallized Ge as a substrate to obtain large grain GaAs films, and the advantage of finely focused laser beams over that of other techniques which give larger area melting in the Ge film. The former technique particularly has the advantage in that the Ge surface is considerably smoother, and less likely to require further treatment prior to GaAs deposition.

Since GaAs growth facilities did not exist at JPL during this reporting period, a sub-contract with Rockwell International was let to grow films of GaAs by organo-metallic CVD (chemical vapor deposition). Most of the growth accomplished was on single crystal GaAs, the polycrystalline GaAs wafers mentioned above, and single crystal Ge. The films, including those grown on polished Ge wafers, were of good quality as indicated by the short-circuit current density of Schottky barrier solar cells fabricated on them.

No GaAs films were grown on Ge substrates recrystallized by line-focused laser beams by Rockwell during this reporting period, but one growth run was performed at Southern Methodist University using HCl-transported Ga CVD. It was found that, as expected, the HCl etching of Ge autodoped the GaAs film with Ge to above 10^{17}cm^{-3} -too high a density to make useful Schottky barrier devices. The etching action also made it clear that the laser recrystallization had not melted the Ge completely through the film thickness-at least not in the regions scanned by the end portions of the laser line. Consequently, the recrystallization system is being converted to a flying spot scanning mode so as to improve the uniformity of Ge melting across the sample.

Considerations of the material availability, material cost, and fabrication steps envisioned for large-scale production which are

amenable to continuous or quasi-continuous processing, are given. It is concluded that sufficient Ga resources are available in aluminum-and zinc-bearing ores to provide at least 10,000 megawatt equivalent GaAs thin-film solar cells per year for up to 40 years, by which time recycling degraded GaAs cells can supply a major part of the required Ga. Development of Ga recovery from coal gasification could double the above annual production rate as well as provide for an indefinite period of production.

The material costs for the major components of the thin-film cell using Ge were projected to be \$0.093 or \$0.140 per peak watt for 15 or 10% efficiency, respectively. These costs projections assumed silicon steel for the substrate, 80% utilization of the semiconductors, 5-and 2-micrometer-thick Ge and GaAs layers, respectively, and present day small-lot material costs. The need for Ni/Fe or graphite substrates would add from 3 to 6 cents per peak watt depending on cell efficiency.

No estimates of capital equipment costs or general operating expenses were made, although with the possible exception of the CVD step, all required process steps are adaptable to automated continuous or quasi-continuous flow.

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SECTION I

INTRODUCTION

Alternative materials and devices for silicon solar cells, which may prove superior either in overall efficiency or in meeting longer-term economic goals even less than the \$0.50 per peak-watt goal, need to be explored. The approach chosen for this program uses polycrystalline gallium arsenide (GaAs) thin films because of their potential for high efficiency and low cost.

Relatively small grain sizes should be acceptable in GaAs films because of their high light absorption. However, since deposited films on low-cost substrates normally have sub-micron grains, which are too small for solar cell application, this program investigated the feasibility of using recrystallized large-grain germanium (Ge) films as an inter-layer between the metal substrate and the chemical vapor-deposited GaAs. The choice of Ge comes from its well-known match to GaAs in lattice parameter and thermal coefficient of expansion. Direct recrystallization of the GaAs film may also prove feasible at some future time allowing for the elimination of the Ge film which adds about 25% to the material cost.

Because of the limited hope that heteroface or heterojunction GaAs solar cells can be eventually fabricated on GaAs polycrystalline films, the AMOS (Antireflection-coated Metal-Oxide-Semiconductor) technology being developed at JPL will be used in this program for the solar-cell structure (Figure 1-1) because of its promise for relatively high efficiency on polycrystalline films.

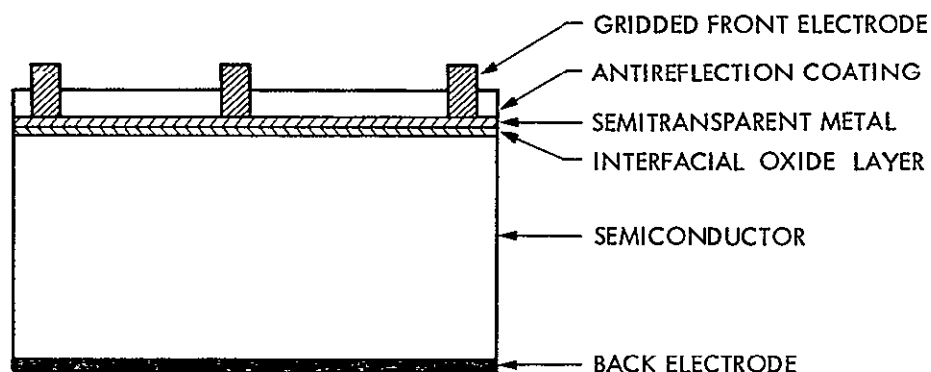


Figure 1-1. Physical Structure of a Single Crystal GaAs AMOS Solar Cell

The final report discusses the several oxidation techniques investigated which have been found to increase the open circuit (V_{oc}) of metal-GaAs Schottky barrier solar cells (Refs. 1,2), the oxide chemistry, attempts to measure surface state parameters, the evolving characteristics of the solar cell as background contamination has been decreased (but not eliminated), results of focused Nd/YAG laser beam recrystallization of Ge films evaporated onto tungsten, and studies of AMOS solar cells fabricated on sliced polycrystalline GaAs wafers. Also discussed are projected materials availability and costs for GaAs thin-film solar cells.

SECTION II

AMOS SOLAR CELL RESEARCH

A. GaAs OXIDATION

1. Sample Preparation

Samples were fabricated on (100) n-type epitaxial GaAs (Te-doped with concentrations ranging from 2×10^{15} to $5 \times 10^{16} \text{ cm}^{-3}$) commercially grown by chemical vapor deposition on Czochralski GaAs substrates. The room temperature Hall mobilities were about $4000 \text{ cm}^2/\text{Volt-sec}$ and minority carrier diffusion lengths measured by scanning electron microscope techniques ranged between 2 and 4 microns. Several boat-grown GaAs samples with carrier concentration about $5 \times 10^{16} \text{ cm}^{-3}$ having (111) orientation have also been investigated.

The wafers were cut to accommodate either a $2 \times 2 \text{ cm}$ sample, a $1 \times 1 \text{ cm}$ sample, or most frequently, four 5-mm circular samples, and initially cleaned with TCE, acetone, methyl alcohol, and deionized water. Ohmic contacts were made by sintering Au-Ge-Ni evaporated contacts for 3 minutes in hydrogen at 480°C . The opposite surface was lapped on a pad with Tizon Lustrox 1200 silicon polish and rinsed with deionized water and methyl alcohol. Next, the surface was chemically etched with 1% bromine in methyl alcohol on nonabrasive lens cleaning tissue in order to remove any work damage from the surface. This last etch, among several etches investigated, was found to leave the minimum thickness of native oxide ($\sim 20\text{\AA}$). The chemical etch was immediately followed by a methyl alcohol quench and deionized water rinse.

Eventually, a change in the polishing pad used was made necessary when the Tizon pads (no longer manufactured) wore out. This caused a deterioration in the AMOS cell characteristics. In fact, baseline cells with no intentional oxide growth could not be made with ideality factors less than about 1.5, whereas previously they had ranged from 1.02 to 1.05.

Consequently, several new chemical etches were investigated in which the Lustrox-polished wafer could be immersed before the final bromine-methanol etch mentioned above. The most promising etch was found to be $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ (10:1:1) followed by either $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (10:1:1) or $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$ (5:1:1). The use of these etches not only lowered the n factors of baseline cells to nearly unity, but also noticeably improved the AMOS solar cells with respect to very low reverse saturation current densities. Details are given in the next subsection.

After oxidation the samples are immediately placed in an oil-free vacuum system, composed of liquid nitrogen-cooled sorption pumps and an Ultek ion pump. The system was modified so that a small chamber holding the sample, sliding evaporation masks, shutters, and quartz crystal film thickness sensor is separately valved so that the minimum pump-down times are only about 5 minutes. The lower chamber of the system contains the evaporation sources; either e-gun or resistance-heated

boats. Only the latter sources were used to avoid the possibility of electrons or ionized particles modifying the oxide characteristics. Gold with 99.999% purity is evaporated to form the Schottky barrier with the thickness ($60 \pm 2\text{\AA}$) controlled by a Kronos ADS-200 digital thickness monitor and relay-actuated shutters. The gold film typically has a sheet resistance of $50\ \Omega/\square$.

The sliding mask fixture allows for a variety of cell geometries and grid patterns to be evaporated sequentially without exposing to the atmosphere if desired. The grid contact on 1 or 4cm^2 samples is composed of an initial gold layer of several hundred $\text{\AA}$ thickness followed by a silver layer evaporated to the desired thickness depending on the lateral dimensions. The grid fingers are one mil in width and ten fingers per cm are used for one solar constant intensities. The entire grid pattern blocks 5-7% of the sunlight depending on the amount of spreading during metal evaporation through the mask. Metal substitutes for the gold layer such as silver, copper, or nickel are desirable for reasons of economy, and probably, for longer lifetimes. Preliminary experiments show a relative insensitivity to the metal type with respect to the enhanced voltage due to the oxide interlayer.

The reflectivity of the Au-GaAs surface is considerable, averaging about 45% over the usable spectrum. The index of refraction of GaAs is considerably modified by the metal film to a degree that cannot be calculated. This is so because the complex index of refraction for metals in thin form is different from that of the bulk form, and more importantly, is dependent on surface properties of the substrate, rate of deposition, etc. Consequently, an ellipsometric technique for evaluating the required optical parameters of a SB solar cell was developed for purposes of calculating the appropriate thickness and index of refraction of an antireflection (AR) coating (Ref. 3). Difficulties with degradation of V_{OC} during the AR coating deposition and means found to prevent it will be discussed in Section II.B.

The GaAs substrates were recycled by repeating the Lustron and Br/methyl alcohol etching steps for a considerable savings in material costs. However, attrition due to breakage, etc., and withdrawal from GaAs growth by Applied Materials, Inc., required a search for new commercial sources. One source* was identified and an order placed for additional substrates.

2. Oxidation Techniques

The oxide layers first reported were grown in air by heating GaAs to $100\text{--}200^\circ\text{C}$ and produced values of V_{OC} between 600 and 650 mV which were not very reproducible (Ref. 1). Increased values between 670 and 750 mV depending on the oxidation technique and crystal orientation were obtained on this task. Reducing background contamination to the minimum amount possible was found to be essential for obtaining reproducible results.

*Epi-Dyne Corp., Hawthorne, CA 90250

It was found that a Br/methanol-etched GaAs surface has a native oxide primarily composed of As_2O_3 with a minimum thickness of 18-20Å. A SB solar cell made on such a surface (baseline cell) is not affected by this layer, except for minor adjustments to the gold barrier height (0.90 ± 0.01 eV on (100) surfaces). Since only about 10Å of additional oxide are being grown, it never has been clear what role the native oxide may play. For this reason and the fact that AMOS solar cells mass produced by automated techniques would probably involve GaAs layers which are freshly grown, and hence, free of any interfacial layer, techniques for removing the native oxide layer by plasma reduction or acid stripping have been tried. Neither approach has been successful. For example, glow discharges using H_2 , CH_4 , various Freons, NH_3 , and HCl were investigated. Although the study should not be considered exhaustive, results were discouraging. Oxidation of freshly-grown GaAs, either in-situ or very soon after growth without prior exposure to external laboratory environments is the next logical step for predicting ultimate potential for AMOS solar cell efficiencies. Plans are being developed for obtaining this capability.

However, as mentioned above, recent experiments with other chemical etches prior to the final Br/methanol etch have shown improvements and some preliminary results are discussed in Section II.B. The following descriptions are for samples prepared by the old recycling techniques.

a. Thermal. The most studied and reliable technique to date for AMOS cells has been oxide growth by low temperature processes. High temperature growths have not been considered since one could not expect to attain the thickness control for the extremely thin oxide layers required. Also, it is known that such oxides are composed primarily of Ga_2O_3 , which is very unstable with respect to its various crystal-line forms. As will be discussed in Section II.C., it was found that a mixture of Ga and As oxides is desirable.

However, at temperatures between room temperature and 200°C , GaAs will not oxidize to a sufficient thickness using dry oxygen alone. Rather it was found that any one of three growth modifiers were necessary: (1) water vapor, (2) ozone, or (3) an organic reactant from the vapor of an epoxy resin (E5 process).

(1) Water Vapor. The highest value of V_{oc} obtained so far with (100) GaAs has been with oxides formed at room temperature by passing water vapor-saturated O_2 over freshly-etched GaAs placed in a quartz tube. Figure 2-1 shows the ellipsometrically-measured oxide thickness and open-circuit voltage as a function of exposure time. As slow as the growth may seem, it is much faster than that found by Lukes (Ref. 4), who obtained 30Å oxide on cleaved (110) GaAs in over 7 days time with exposure to air with no special humidity control. The highest values of V_{oc} were about 800 mV (28°C), whereas other oxidation techniques to be discussed led to a value between 670-700 mV on (100).

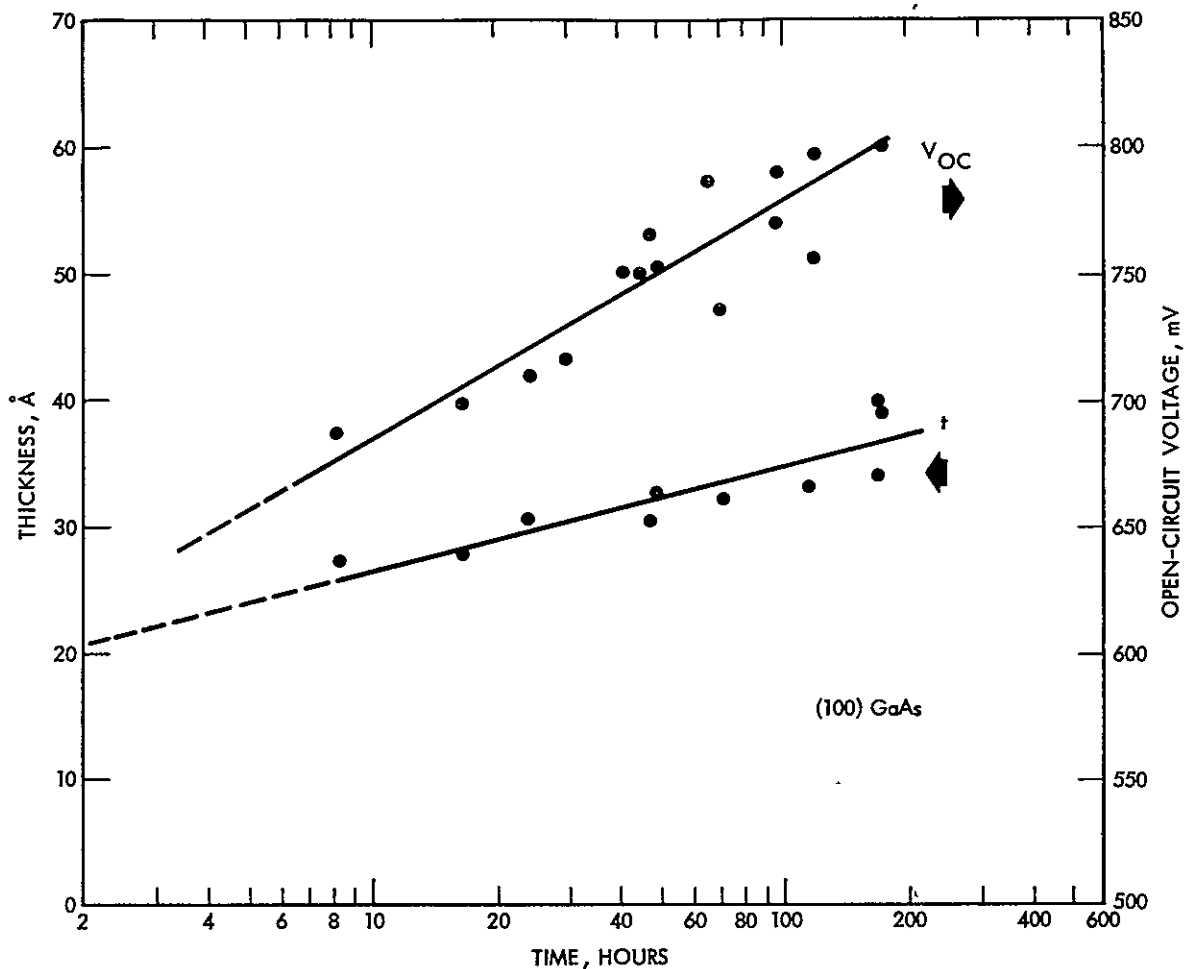


Figure 2-1. Dependence of Oxide Thickness (t) and Open-Circuit Voltage (V_{OC}) on Time of Exposure to Water Vapor-Saturated Oxygen at Room Temperature

surfaces.* Similar studies are soon to be made at slightly elevated temperatures (40° and 60°C) when new GaAs material is available. Temperatures above 80°C during oxidation caused desorption of As_2O_3 .

It should be noted that values of V_{OC} given here are not definitive for any one oxidation technique. Most results in this report are for samples metallized with the standard 60 $\text{\AA}$ gold film, but which do not

*There are orientation effects for all oxidation processes and values of V_{OC} well above 700 mV are also obtained on (111) Ga-rich surfaces, for example.

have AR coatings. The AR coating increases V_{oc} by nearly 20 mV because of an increase in short-circuit current by 60%. However, the application of the coating by vacuum deposition partially reduced the oxide-enhanced voltage by 100 to 150 mV, especially for the case of samples with initially very high V_{oc} , (~750 mV). Means found to prevent this are discussed in Section II.B.

(2) Ozone. Much faster oxidation rates are obtained with ozone (O_3) passing over heated, freshly-etched GaAs. The ozone is obtained by passing oxygen vapor from liquified oxygen through a gas discharge chamber at a flow rate of 1 ft³/hr. Optimum parameters are 20 minutes at 120°C which leads to oxide thickness of about 30-32Å, although the exact time of exposure or temperature is not critical. At a temperature of 120°C, times shorter than about 15 minutes gave smaller V_{oc} values, while times longer than about 60 minutes caused the fill factor (usually 75-80%) to decrease, probably because of increased impedance to the current flow by the oxide layer. Performing all sample handling steps within a clean-bench environment, including the loading into and unloading from the tube furnace, was again found to be a minimum precaution for reproducibility. Typical values of V_{oc} were 680, 730, and 630 mV for uncoated cells fabricated on (100), Ga-rich (111), and As-rich (111) surfaces, respectively, showing a strong orientation effect.

The O_3 -generating apparatus used for the above results broke down due to deterioration of insulators within the apparatus. AMOS solar cells fabricated since have not given comparable results. Consequently, this activity was temporarily suspended.

(3) E5 process. The third thermal oxidation process again uses oxygen, but with an organic reactant in place of the water vapor as an oxide growth modifier. Undoubtedly a wide range of such reactants exist, but it was found that the vapors from the resin of an epoxy placed within the heat zone will work. The active component of the resin has not been identified. The electrical characteristics of AMOS cells made with this process are very similar to earlier cells using O_3 . Since the optimum time (90 minutes) and temperature (160°C) are greater than required for the O_3 process, and since the nature of the process appears to preclude exact control of the active reactant, the E5 process was discontinued relatively early in the reporting period.

b. Glow Discharge. Another oxidation process using low energy oxygen plasma was also initiated. This process is particularly attractive from a production point-of-view because of its speed and the fact that it can be done at room temperature. The gas discharge apparatus is energized by a RF field surrounding a 3-inch Pyrex envelope pumped by a zeolite cryo-sorption pump. The oxide growth rate was found to be extremely rapid even for RF energies of about 1 watt and oxygen partial pressures as low as 30 microns. Runs lasting over a minute grew oxides that exhibited hysteresis in the dark and light current-voltage (I-V) curves, and had very poor fill factors, and reduced current outputs.

However, runs lasting between 10-20 seconds gave values of V_{oc} comparable to O_3 oxidations on (100) surfaces, although not as high on (111) surfaces.

A smaller quartz tube in which to place the sample was inserted within the Pyrex envelope in order to slow down the reaction rate for finer control and to shield the GaAs surface from contamination from the chamber walls. Oxide growth rates were reduced by more than an order of magnitude. The same apparatus was unsuccessfully used for attempts to remove the native oxide as referred to earlier, using a variety of etchant gases.

c. Anodic. A variety of anodic techniques, both aqueous and non-aqueous, have been developed at other laboratories for growing relatively thick oxide layers on GaAs. The growth of 30Å oxides by such techniques do not appear to be attractive for several reasons: (1) difficult thickness control since growth rates are sensitive to the degree of stirring and since reported growth rates are typically quite high, (2) difficult uniformity control especially if no stirring is used for the reason given in (1), (3) the fact that arsenic oxides are soluble in water, and (4) process complexity as compared to thermal or plasma techniques-particularly for large production rates.

However, before ruling out anodization as a viable process, one each of an aqueous and non-aqueous technique was investigated. The inherent high growth rates were substantially reduced by increasing the series resistance of the circuit.

(1) Aqueous. The electrolyte used was a 3% aqueous solution of H_3PO_4 buffered to a pH of about 6 with NH_4OH . This solution was then mixed with ethylene glycol in a ratio of 1:2. The use of glycol recently was reported to solve earlier problems with regard to sensitivity to the solution pH and instability against impurities and gold deposition (Ref. 5). With a constant voltage of 45 volts applied (GaAs cathode) and an external series resistance of eleven megohm, growth rates of $\sim 4\text{\AA}/\text{min}$ were obtained with an anodic current of $1.32\text{ }\mu\text{A}/\text{cm}^2$. A 20-sec rinse with high purity water dissolves 10-20Å oxide. Even a methanol rinse alone was found to remove some of the oxide; hence, the thickness control is difficult, as expected.

(2) Non-aqueous. In order to grow anodic oxides which will not be affected by water in the electrolyte or rinse, a saturated acetone solution of reagent grade $KMnO_4$ mixed at room temperature to which electronic grade acetone is added in the ratio of 1:25 was tried (Ref. 6). Rinses were with acetone followed by dry nitrogen gas drying.

The growth rates were noticeably faster than with the aqueous solution using the same circuit and applied bias. With the same setup as used above and 15V bias, 100Å oxides could be grown in 5 minutes. In fact, the contact potential difference between the GaAs and the Ta back plate, upon which the samples were mounted in order to reduce breakage, was sufficient to maintain oxidation without an applied bias.

Even in this case, high series resistance was required in order to minimize oxide thicknesses to levels that did not seriously impede the minority carrier flow. Most AMOS cells made with this process required less than 1 minute within the solution using zero bias, no stirring, 500 K Ω or more resistance, and illumination from a high intensity lamp.

B. SOLAR CELL CHARACTERISTICS

1. General

In order to best see the enhancement in efficiency that the oxide layer can provide to a SB GaAs solar cell, the characteristics of the baseline solar cell are reviewed first (Ref. 7). Curves 1-3 in Figure 2-2 show light I-V curves for such cells fabricated on (100), $\bar{1}\bar{1}\bar{1}$, and (111) surfaces, respectively. The diode parameters n and reverse saturation current densities J_0 are given in Table 2-1. The current outputs of $\bar{1}\bar{1}\bar{1}$ cells are lower because the boat-grown GaAs had shorter minority carrier diffusion lengths than those measured in the (100) epitaxial GaAs (2-4 μm). When AR coated, the current densities in epitaxial GaAs are increased by 60-65% (Ref. 3) to a value of about 25 mA/cm² for a gridded cell exposed to 100 mw/cm² intensity light from an ELH lamp simulator calibrated with a standard silicon solar cell for AM1 operation. Measurements in outside sunlight gave ampere per watt values within several percent of the above.

The values of V_{oc} are seen to range from 460 to 510 mV for the three orientations. The variations are due to some differences in barrier height (as measured by photoelectric response) and in the empirical n -factor in the dark I-V characteristic. These differences, in turn, are probably due to the different etching reactions of the surfaces to the chemical etching, leaving somewhat different interfacial state densities at the native oxide-GaAs interface. Before the trouble with worn polishing pads, both the (100) surface and (111) A surface had "true" SB characteristics in that the n -factor could be made as low as 1.02 and the value of reverse saturation current density J_0 was exactly equal to the current density calculated for the value of barrier height measured by photoelectric response, using the expression

$$J_0 = A^*T^2 \exp(-\phi_B/kT), \quad (2-1)$$

where A^* is the modified Richardson's constant equal to 8.6 Amp/cm²/°K² for GaAs, and ϕ_B is the barrier height measured from the metal Fermi level. Cells fabricated on $\bar{1}\bar{1}\bar{1}$ B surfaces with the original etching techniques could not be made with n factors lower than 1.08. With the new chemical etches used for recycling GaAs surfaces mentioned above, the same ideal SB characteristics were again obtained on (100) surfaces. Other orientations have since not been reinvestigated.

From the usual solar cell equations

$$J = J_D - J_L, \quad (2-2a)$$

$$J_D = J_0[\exp(qV_D/nkT) - 1], \quad (2-2b)$$

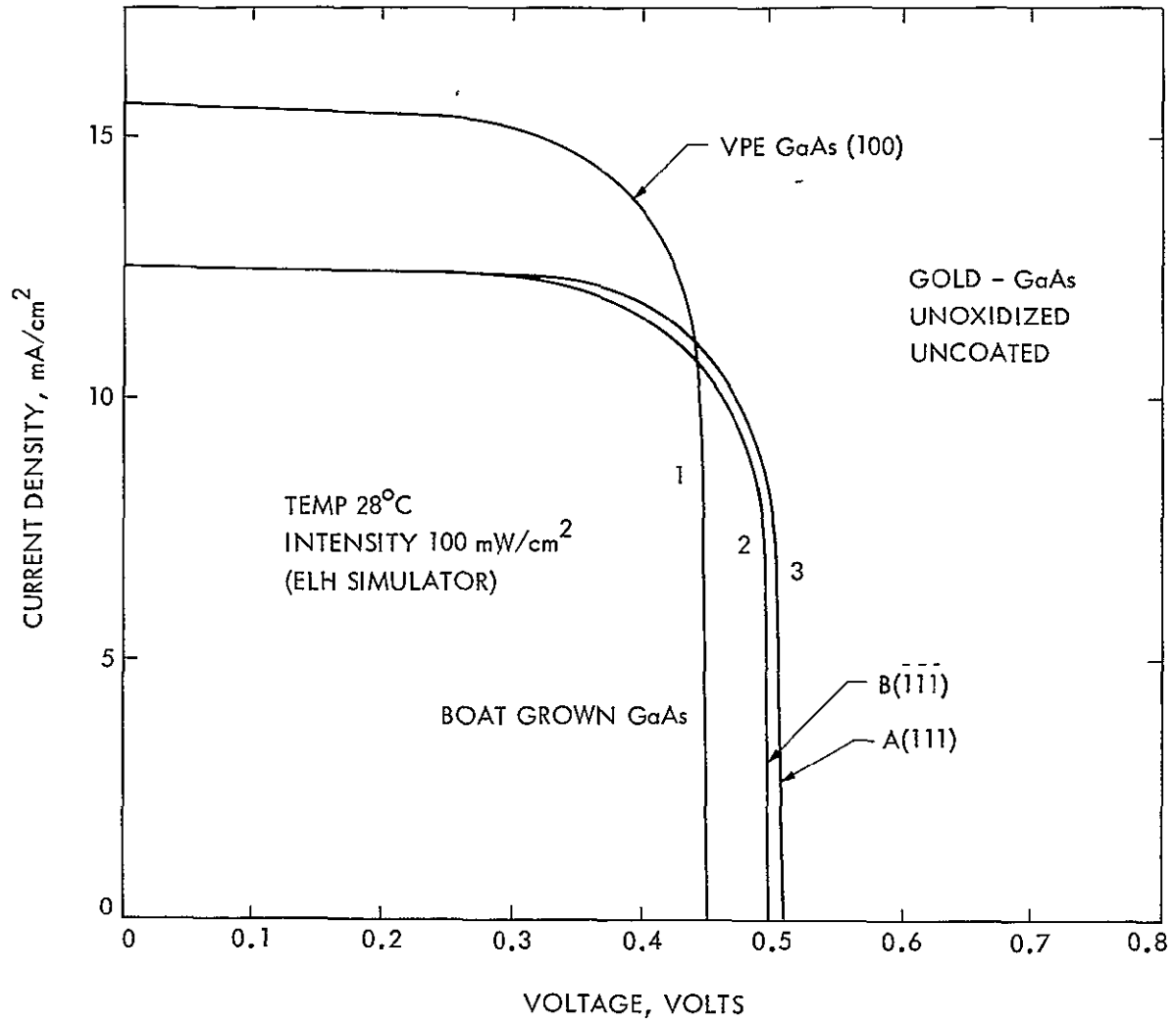


Figure 2-2. Light I-V Characteristics of GaAs Baseline (No Oxide) Solar Cells for Three Crystal Orientations

and Eq. (2-1), the open-circuit voltage can be expressed as

$$V_{oc} = \frac{n\phi_B}{q} + \frac{nkT}{q} \ln \frac{J_L}{A^*T^2} . \quad (2-3)$$

In these expressions, q , k , and T have their usual meaning, J_L is the light-generated current, and V_D is the algebraic sum of the applied voltage and voltage drop across the series resistance R_S . At $T=28^\circ\text{C}$ and

Table 2-1. Photovoltaic and Diode Parameters for Cells Used in Figures 2-2 and 2-3

CURVE	ORIENTATION	OXIDATION	Φ_B (eV)	J_0 (A/cm ²)	n	V_{oc}^a (mV)	FILL FACTOR ^b (%)
1, Figure 2-2	100	NONE	0.900	7.3×10^{-10}	1.02	462	74.8
2, Figure 2-2	A(111)	NONE	0.975	4.0×10^{-11}	1.02	498	74.8
3, Figure 2-2	B($\bar{1}\bar{1}\bar{1}$)	NONE	0.936	2.0×10^{-10}	1.08	510	76.1
1, Figure 2-3	B($\bar{1}\bar{1}\bar{1}$)	O ₃ , 120°C	1.035	1.5×10^{-9}	1.85	655	68.3
2, Figure 2-3	(100)	O ₃ , 120°C	1.025	5.9×10^{-12}	1.15	680	78.1
3, Figure 2-3	A(111)	O ₃ , 120°C	1.032	8.3×10^{-11}	1.56	741	73.1
4, Figure 2-3	A(100)	O ₂ , + H ₂ O, RT 114 HOURS	1.033	1.0×10^{-10}	1.40	758	78.5

^aMEASURED AT 28°C WITH 12.5 - 16 mA/cm² LIGHT-GENERATED CURRENT DENSITY.

^bFILL FACTORS ARE SOMETIMES LIMITED BY THE FACT THAT NO GRID CONTACT HAS BEEN USED.

a current density level of 25mA/cm² for a coated cell, Eq. (2-3) can be written as

$$qV_{oc} = n(\phi_B - 0.447) \text{ (eV)}. \quad (2-4)$$

Thus, in a SB solar cell, the barrier height is the major parameter for maximizing V_{oc} , and hence, efficiency. The relationship given by Eq (2-3) is independent of base resistivity* as long as the carrier concentration is lower than $\sim 2 \times 10^{17} \text{ cm}^{-3}$ in order to preclude mixed thermionic-field emission current transport or as long as secondary channels of conductance are not introduced, such as by the addition of interface states which may act as recombination centers. Either case would cause J_0 to be larger than predicted by Eq. (2-1). Indeed, the latter case was generally common because samples prepared with the newer chemical etches exhibit reverse saturation currents as much as two decades lower than measured in samples made until recently using the older chemical etching.

When the GaAs surface is oxidized, the value of V_{oc} increases by 50-60% depending on the oxidation technique and surface orientation. Figure 2-3, for example, gives some light I-V curves for ozone-treated (100), (111) and $(\bar{1}\bar{1}\bar{1})$ GaAs (120°C, 20 minutes) and for a (100) surface oxidized by water vapor-saturated O₂ at room temperature for 114 hours. The corresponding dark I-V characteristics are shown in Figure 2-4. Table 2-1 lists several diode and photovoltaic parameters for each sample type. These samples had been etched by the older technique described earlier.

Typical oxide thickness range from 30-35^oÅ as measured by ellipsometry.** The large difference in V_{oc} between the Ga-rich and As-rich (111) surfaces are probably, at least partially, due to differences in the native oxide initially present before oxidation. The conversion efficiencies of these devices when AR coated would range between 9.3 and 15.8% (Curves 1 and 4). The higher range of efficiencies are, of course, obtained with the better quality epitaxial GaAs.

The change in V_{oc} caused by oxidation occurs by two mechanisms. First, the barrier height of 0.90 - 0.975 eV in baseline cells is increased to about 1.03 ± 0.01 eV for any one of the oxidation processes described earlier. Each of the three surface orientations investigated have similar values for ϕ_B after oxidation within ± 0.01 eV. The increased barrier height may come about from a modification of the surface states

*In practice, the lowest carrier concentration obtainable is utilized in order to maximize current output by means of the increased space-charge region volume for carrier generation and by the usual concomitant increased minority carrier diffusion length for carriers generated in the neutral region of the semiconductor.

**Significant amounts of carbonaceous material were observed on the oxide surface by ESCA measurements. This may in turn lead to somewhat exaggerated oxide thickness as measured by ellipsometry

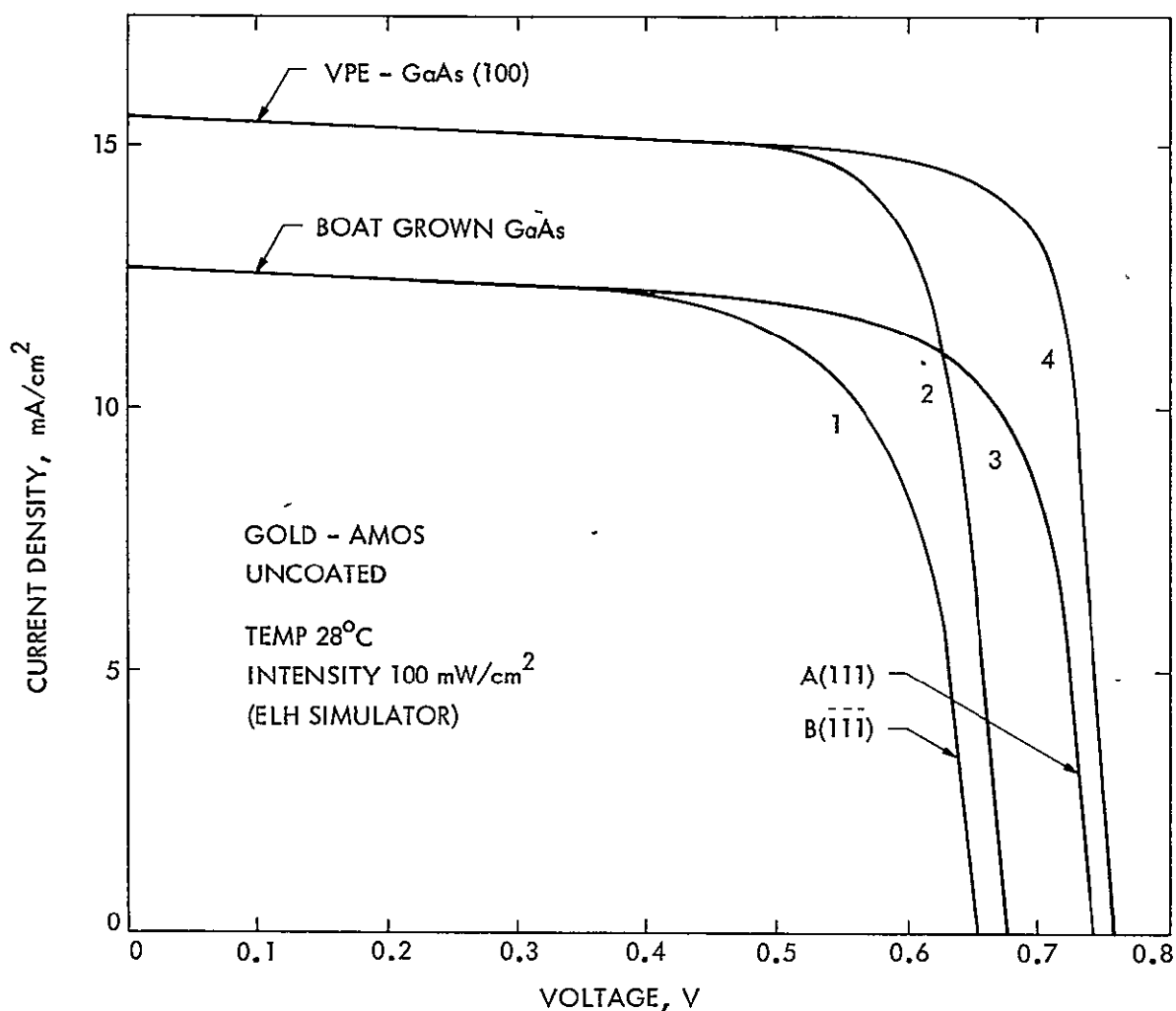


Figure 2-3. Light I-V Characteristics of AMOS Solar Cells with the Oxide Formed by O_3 (Curves 1, 2 and 3) and with O_2 /Water Vapor (Curve 4) (See Table 2-1)

which are known to control the barrier heights in most metal-semiconductor systems (Ref. 8), or by the presence of negative charge within the oxide layer which would increase the positive space charge within the depletion region. This effect accounts for up to 150 mV of the increase in V_{oc} .

The second mechanism increasing V_{oc} is a modification of the majority carrier transport over the barrier causing the diode n factor to increase (Refs. 9-11). As seen from Eq. (2-3), the value of V_{oc} is directly proportional to n . However, Eq. (2-3) is valid only if the

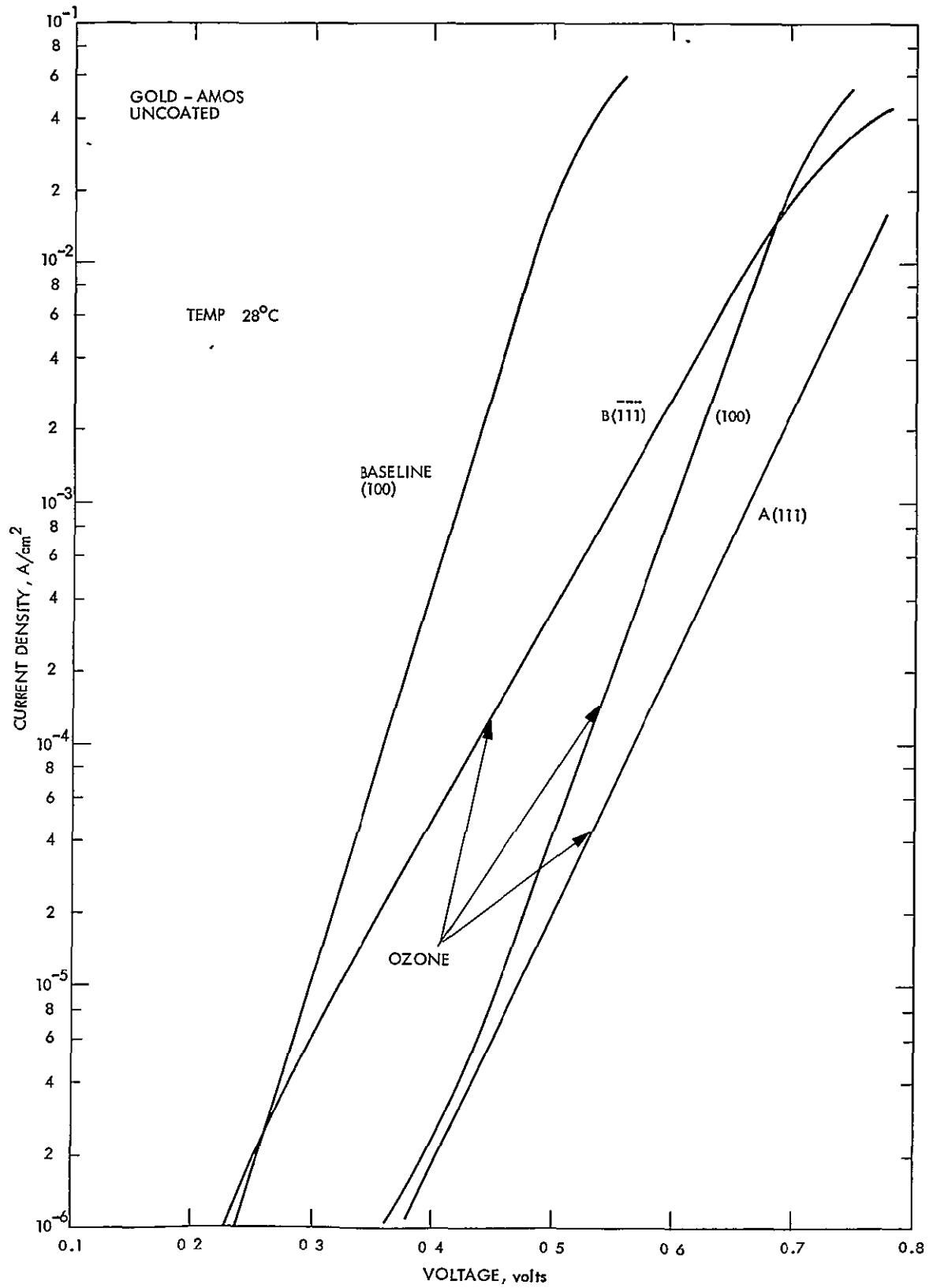


Figure 2-4. Dark I-V Characteristics Baseline Solar Cell and AMOS Solar Cells Shown in Figure 2-3 (See Table 2-1)

reverse saturation current is limited by thermionic emission over the barrier. In practice, the value of J_0 usually increases with the addition of an oxide layer, partially offsetting the expected improvement in V_{oc} . This was particularly the case for the AMOS solar cell when first reported (Ref. 1). At that time, no barrier height increase was detected, n factors were $\sim 1.8 - 2.0$, and excessive reverse saturation currents were measured. The latter was probably due to the addition of secondary channels of conductance due to tunneling to and from surface states or traps in the oxide layer, recombination at the interface states, or minority carrier injection. The reasons for the added conductance are not known, but were probably related to the surface preparation and degree of background contamination.

Besides increasing the barrier height, the oxidation of (100) GaAs described above also raised the n factor from unity to 1.15-1.20 without affecting J_0 , i.e., the measured value of J_0 is equal to that calculated from Eq. (2-1) using $\phi_B = 1.025$ - the enhanced barrier height. Consequently, the AMOS solar cell on (100) GaAs still has the characteristics of a Schottky barrier. AMOS cells fabricated on the Ga-rich (111) surface also have similar characteristics with J_0 only about one order of magnitude larger than expected for its measured barrier height, but with values for n of 1.4 - 1.6. It is high value of n without a serious increase in J_0 that accounts for the highest V_{oc} values occurring on (111) A surfaces (for O_3 -generated oxides). By contrast cells made on As-rich ($\bar{1}\bar{1}\bar{1}$) surfaces, though having even larger n values, exhibit three orders of magnitude increase in J_0 , and consequently, a V_{oc} value less than that on (111) cells by nearly 100 mV. Whether this is intrinsic to the crystallography or due to difference in initial native oxides is yet to be determined.

As stated earlier, AMOS solar cells made most recently using the sulfuric acid or ammonium hydroxide-based etches show yet another regime of current-voltage characteristics. To date only oxides grown by room temperature exposure to water vapor saturated with O_2 have been investigated for wafers recycled with these newer chemical etches. These cells have shown even further decreased reverse saturation current densities-as low as 6×10^{-14} A/cm²! However, the n values have also decreased (1.04 - 1.10) so that the values of V_{oc} are still in the range of 700-800 mV. An example of such a cell is shown in Figure 2-5. Note the high fill factor (FF) of 0.811. When AR coated, the efficiency would be 14.5%. The trend of lower values of J_0 , which may continue as cleaner oxide-GaAs interfaces are grown, is desirable in that higher fill factors are obtained due to the lower values of J_0 . Figure 2-6 shows the increase in FF, as well as V_{oc} and efficiency, as J_0 decreases for the case of a representative cell with a response of 0.25 ampere/watt. If the value of n is larger than unity, which it is by at least 5 to 10%, the efficiency and value of V_{oc} is increased by the factor n while the fill factor is unchanged.

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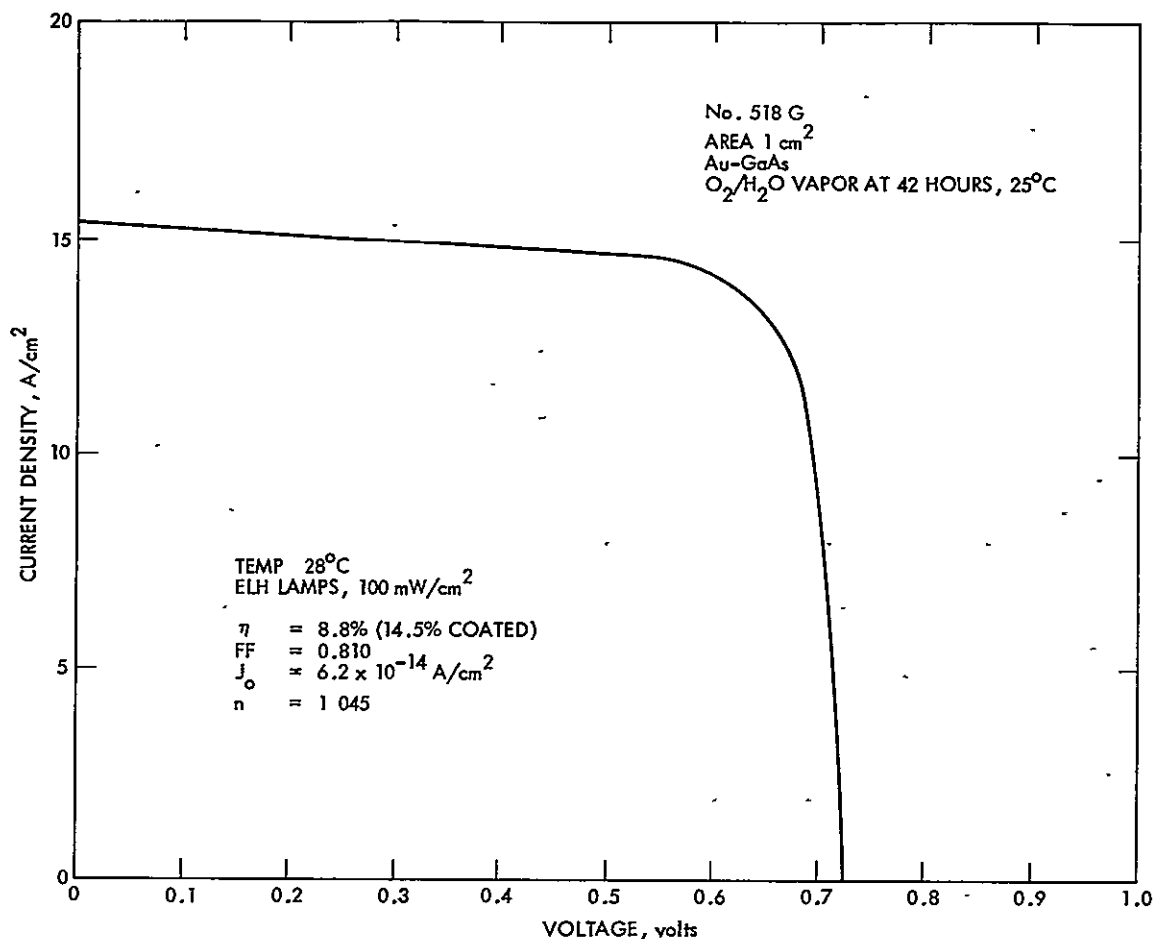


Figure 2-5. Light I-V Characteristics of an AMOS Solar Cell
Using Improved Chemical Etching Before Oxidation

2. Degradation

a. AR Coating. As mentioned in Section II.A., values of V_{oc} were not definitive for any particular oxidation technique. Most results were for samples metallized with the standard 60Å gold film without AR coatings. The AR coating would have increased V_{oc} by about 20 mV through an increase of 60% in short-circuit current. However, in the past, the application of the AR coating tended to reduce the oxide-enhanced voltage by 100-150 mV, especially for the case of samples with initial high V_{oc} (~750 mV). It is believed that the reduction in V_{oc} is caused by heat-induced migration of free metal atoms through microcracks or open areas in the oxide neutralizing interface charge which may be contributing to the enhanced barrier height. Heating of the cell by exposure to the hot evaporation source and by latent heat

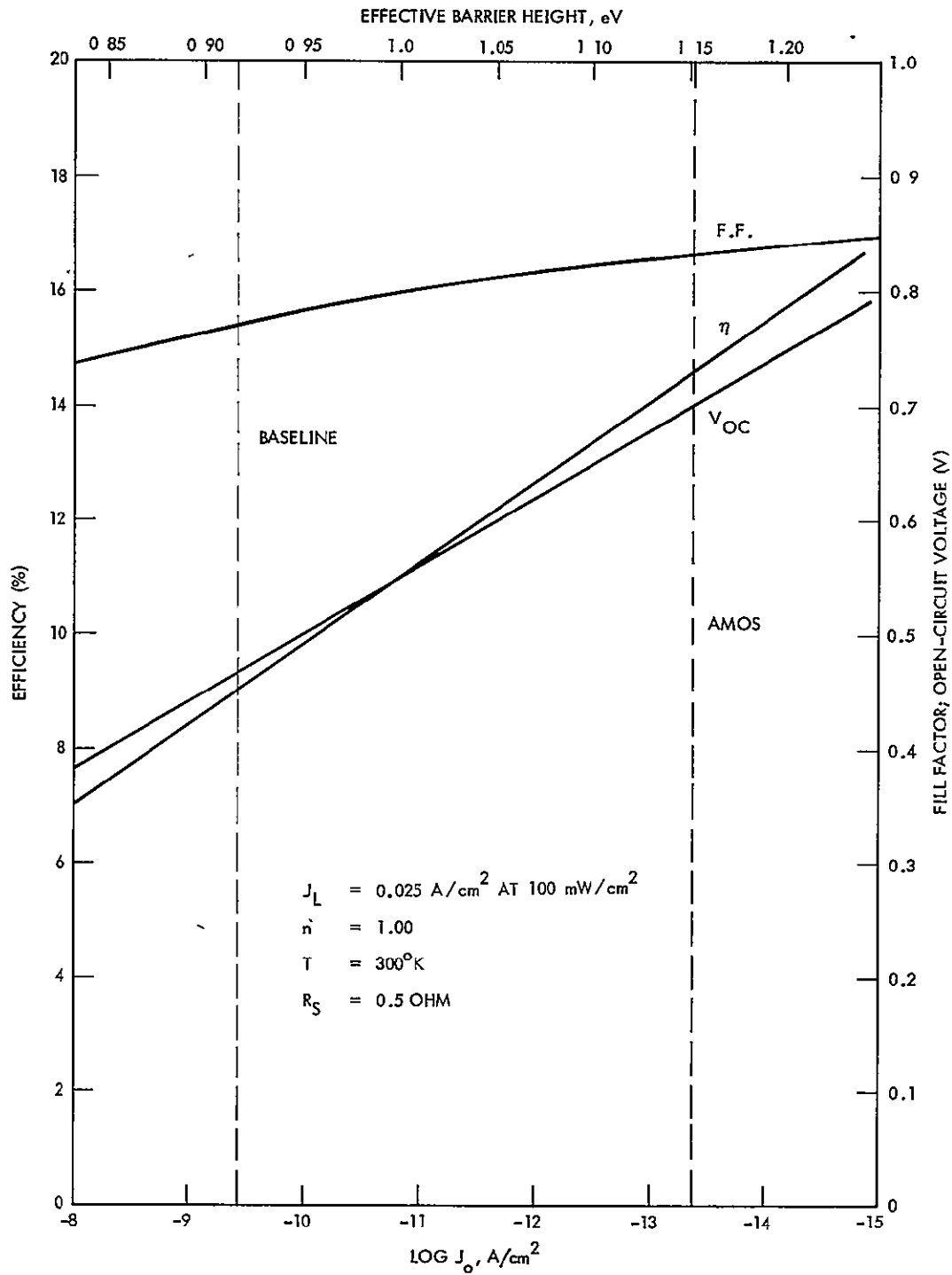


Figure 2-6. Dependence of V_{OC} , Fill Factor and Efficiency (η) on Reverse Saturation Current Density J_0

of condensation probably accelerates the migration. Heat alone was determined not to be the cause.

In order to eliminate this effect, low temperature AR coating techniques were investigated. Initially, the technique of cooling the substrate during the AR coating deposition process was employed. Various high refractive index oxides have been deposited by an E-gun or a resistively-heated boat, in an oil diffusion-pumped system with liquid nitrogen Meissner trap, on cooled samples with no success. It was suspected that water vapor or some other condensable impurity, condensed on the sample surface during the cooling process, degrading the cell performance.

Near the end of this reporting period, it was found that vacuum deposition of Sb_2O_3 using a pulsed TEA CO_2 laser (Figure 2-7) caused no V_{oc} degradation in AR-coated solar cells. Pulsed laser evaporation should have minimum heating effect as well as the least possible change in stoichiometry of the evaporant. In fact, V_{oc} increased slightly after the Sb_2O_3 AR coatings were deposited by the laser as expected from the higher short-circuit current. The success of this new approach is clearly shown in Figure 2-8. Several other oxides were tried using pulsed laser vacuum deposition; however, control of deposition parameters was difficult. This was apparently due to sudden change of the reflectance as the oxide surface changes from solid to liquid phase during laser heating. (Sb_2O_3 sublimates from the solid phase.) Hence, the amount of power coupled into these oxides drops as the oxides melt, causing temperature instability and erratic deposition rates. A rotating crucible holder may resolve some of these problems.

Additionally, Sb_2O_3 was successfully deposited from a resistively-heated crucible. This approach is usually about as effective as the laser deposition technique. Only occasional, small degradation (10-20 mV) after Sb_2O_3 is deposited from a resistively-heated crucible was observed. In summary, the degradation of V_{oc} due to AR coating process has been minimized and is no longer considered a limiting factor in the AMOS solar cell performance.

b. Thermal. AMOS solar cells without the protection of an AR coating generally showed slow degradation in V_{oc} as well as in FF when they were exposed to humid laboratory air for prolonged periods of time, whereas cells with an AR coating show no apparent degradation when they are in air for months. Similarly, uncoated AMOS cells stored in a desiccator showed no degradation. In order to accelerate other degradation processes and to study the high temperature performance of the AMOS solar cells at the same time, elevated temperature tests were performed. Preliminary results showed that AMOS solar cells heated to 115°C in air resulted in some irreversible degradation of V_{oc} (about 80 mV reduction after heat treatment). Similar experiments performed on baseline Au-n-GaAs solar cells also showed some irreversible degradation. There is strong indication that this degradation may be due to gold and gallium interdiffusion (Ref. 12). In future work, plans are to investigate the stability of AMOS solar cells using metals other than gold. Since the Al/GaAs (Ref. 12, 13) SB systems were shown to be stable at high temperatures,

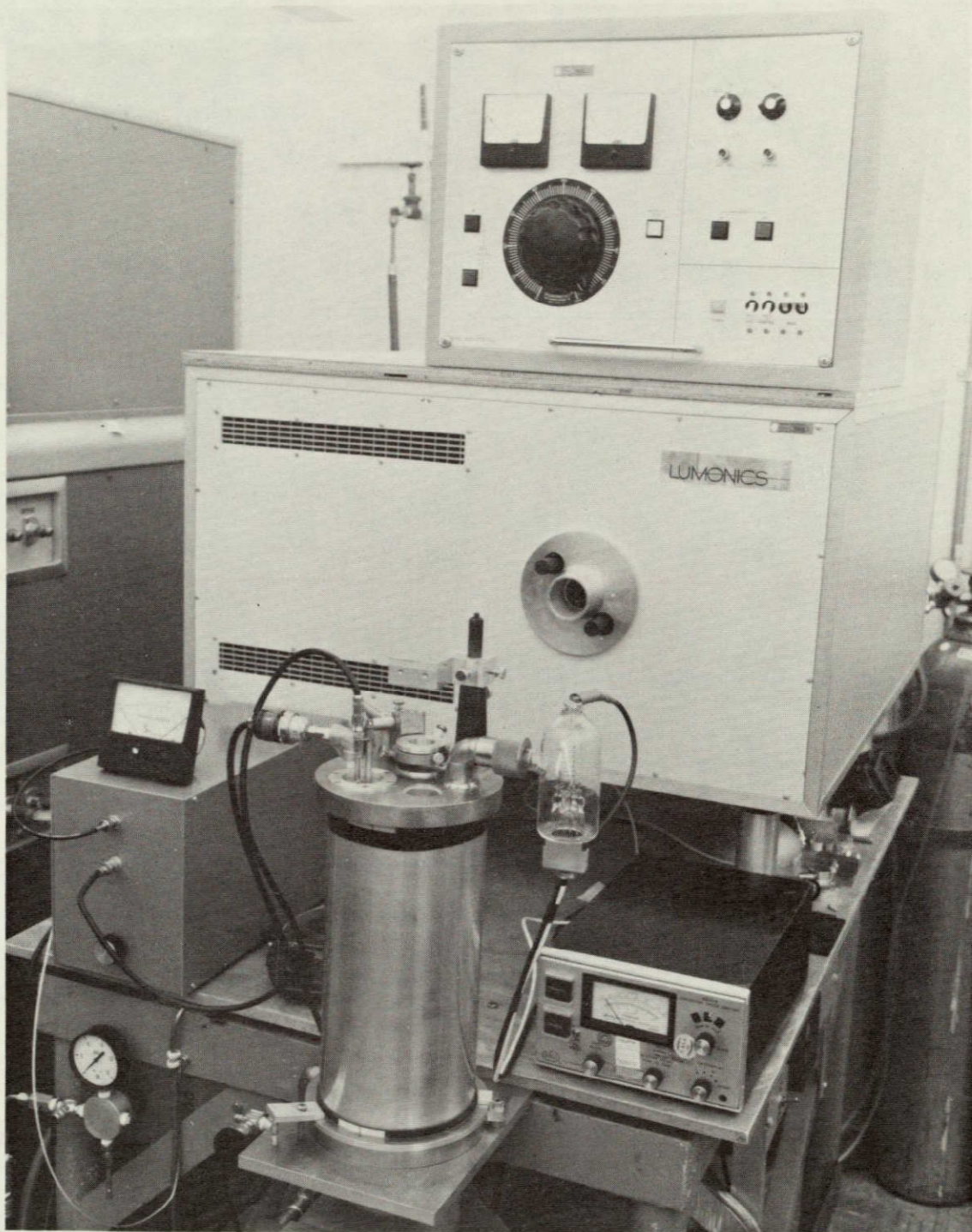


Figure 2-7. Photograph of TEA CO₂ Laser and Test Evaporation System for Antireflection Coating Deposition

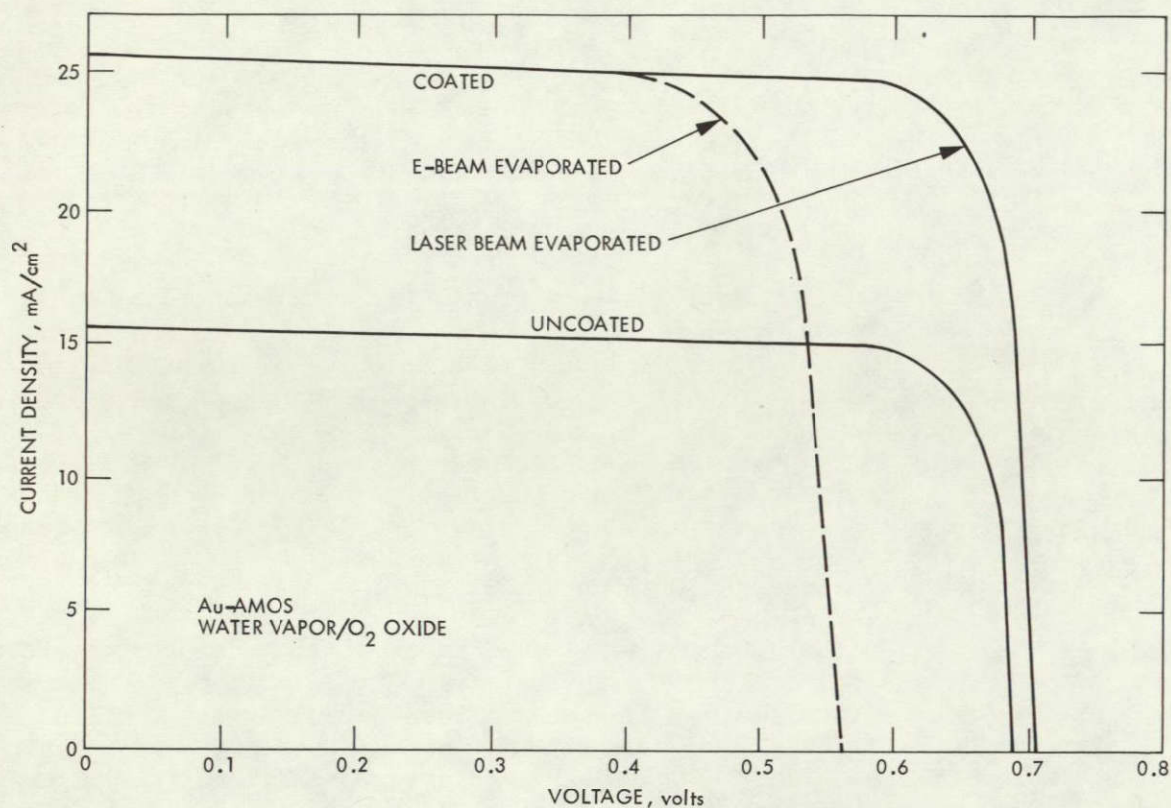


Figure 2-8. Light I-V Characteristics Showing the Differences Between Laser Flash-Evaporated and e-Beam Evaporated Antireflection Coatings

Al will be first examined for AMOS cells. Other conducting materials with a low diffusion coefficient in GaAs or which allow little Ga or As penetration through the metal will also be explored.

Since thermal degradation may also be due to changes in the interfacial oxide layer, additional experiments will be conducted to clarify this possibility for various oxide preparations using Auger and XPS techniques.

C. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

To determine the chemical composition of oxides grown on GaAs, and to understand and control the oxide growth process, a number of studies using XPS were instituted. A description of the instrumentation was given in the Third Interim Report. A brief summary of preliminary

results are given here. More detail will be published elsewhere (Ref. 14) and is given in Appendix A.

The probing depth of the XPS method is determined by the photoelectron mean-free path, which is approximately 30-40Å for most oxides. With suitable signal recovery techniques, the chemistry of the oxide, substrate, and oxide/substrate interface can readily be investigated with an oxide thickness of up to about 80Å. A few photoelectron spectra have also been obtained from the gold-oxide interface with a 60Å-thick gold layer as used in SB solar cells.

Examination of baseline cells (i.e., with no intentional oxide layer), using Br/methanol etch only, showed residual carbon and nitrogen species on the surface, together with an oxide of about 20Å thickness which was predominantly As_2O_3 . Ellipsometric measurements confirm the presence of the 20Å native oxide. Figure 2-9 shows several XPS scans in the As 3d region of GaAs surfaces with no gold metallization, including one scan for the baseline surface. All samples were transported to an introduction chamber in evacuated dessicators. The sample introduction chamber, pressurized with high-purity nitrogen, has a water vapor and oxygen concentration below 0.1 ppm.

Surfaces oxidized by O_2 and water vapor at room temperature have arsenic oxides predominated by the trioxide at 3.2 eV above the substrate binding energy, while ozone-generated oxides predominantly contain As^{+5} 4.4 eV above the substrate binding energy (Fig. 2-9). The latter oxides contained about 1.5 times as much arsenic oxide as gallium oxide (Ga_2O_3) on (100) and As-rich ($\bar{1}\bar{1}\bar{1}$) surfaces. However, on Ga-rich (111) surfaces, which when metallized give the highest V_{oc} , the ratio of arsenic to gallium oxides is only 1.0 or even less. Whether the higher voltage observed on (111) surfaces is dependent upon the lower ratio or is merely due to differences in the residual native oxide after the Br/methanol etch is unknown. It should be noted, however, that the (100) surface oxidized with water vapor and O_2 at room temperature also showed a low arsenic oxide to gallium oxide ratio (0.85), having very little native oxide initially. Cells made on this surface have shown the highest V_{oc} values to date.

D. SURFACE STATE AND OXIDE CHARGE

1. Introduction

Investigation of the feasibility of characterizing interface states and oxide charge is being performed on a subcontract to Pennsylvania State University awarded in May, 1976.

Various measurement techniques for obtaining information on localized states in GaAs-oxide structures and for obtaining information on transport mechanisms in M-I-S structures are being explored. Capacitance C_p and conductance G_p measurements as functions of frequency and bias were given the most emphasis. To obtain meaningful forward-bias C_p and G_p data, an instrumentation system was evolved after considerable effort.

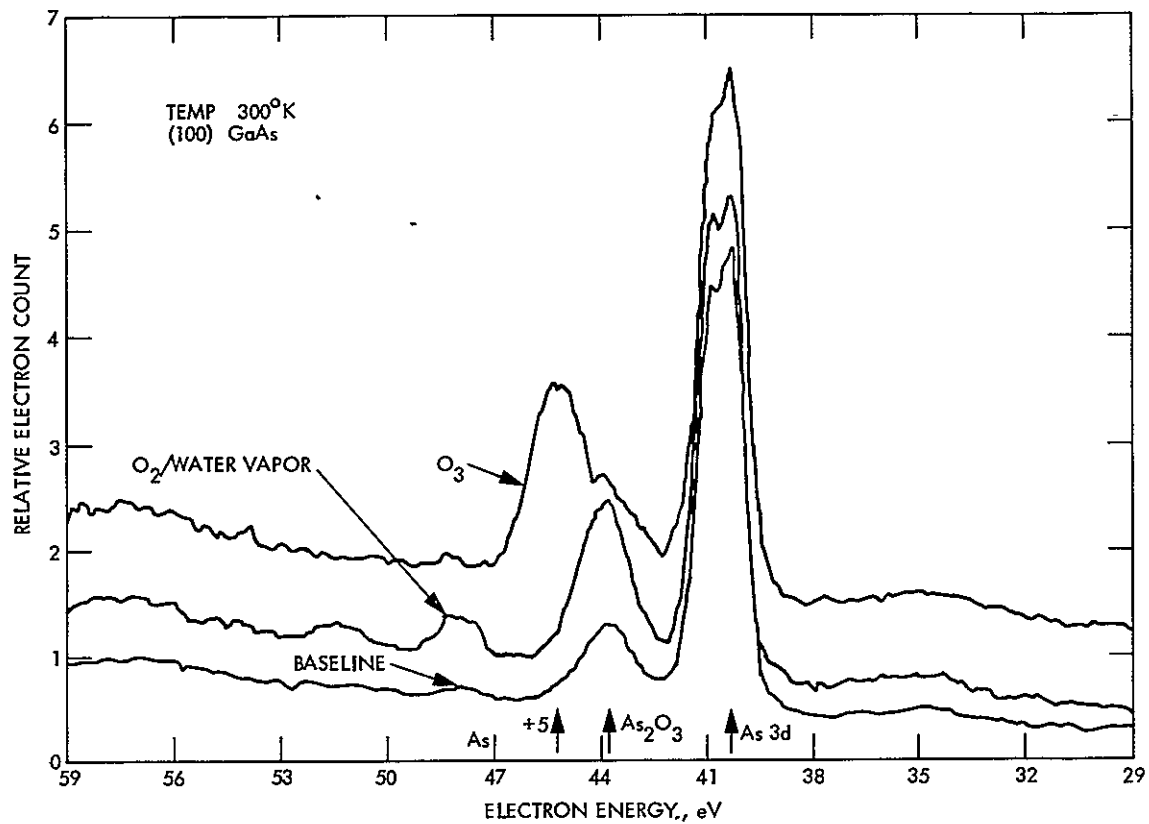


Figure 2-9. XPS Scans of the As 3d Region for a Chemically-Etched Baseline Surface and Surfaces Oxidized With O₃ at 120°C and O₂/Water Vapor at 23°C

Analytical work and theoretical modeling were also undertaken to develop tools for interpreting C_p and G_p data correctly. Finally these efforts have culminated into some ability to explore GaAs AMOS devices, fabricated by various procedures, and to correlate their performance with transport and localized state information.

2. Approaches

Several approaches to characterize GaAs-oxide interface parameters are in various stages of examination. These approaches and the results obtained are as follows:

(a) Bias-temperature stress measurements for mobile ion detection. This test has received a preliminary examination. For the parameters chosen (300°C, 10 volts reverse bias) substantial changes

occurred in device performance. Additional runs with varied conditions must be undertaken to determine the cause, when more material for device fabrication is available.

(b) Transient currents and capacitance measurements. This approach is now in the state where most of the equipment has been assembled with some components on order.

(c) Capacitance-conductance measurements. The measurement of C_p and R_p at various frequencies and biases conceptually allows for comparing one fabrication process with another. It affords the possibility of obtaining "signatures" characteristic of each oxide fabrication process. It also may afford information as detailed as localized state distributions in energy, their capture cross-sections, etc. Consequently, after setting up GaAs furnace facilities, etc., most of the efforts concentrated on this approach.

Basically C_p and R_p of the M-I-S solar cell structure can be obtained either by a bridge approach or by a lock-in amplifier approach. The former suffers from the fact that the few bridges which might be able to handle the large C_p and R_p values expected from M-I-S solar cell structures in forward bias would require the use of small dots or the modification of the bridge standards. Further examination of bridges with a reasonable cost (less than \$5,000) showed that there are, at most, a couple of bridges which may be able to handle the C_p and R_p values of these cells in forward bias. One of these was received from General Radio for evaluation on a trial basis.

It would be better to obtain R_p and C_p values for "signatures" and for detailed energy and capture cross-section analyses from structures used in solar cell studies rather than from small dots fabricated for R_p and C_p measurements in order to avoid possible edge effects. For this reason, it was decided to have the primary effort for obtaining $R_p = R_p(V, \omega)$ and $C_p = C_p(V, \omega)$ data in the lock-in amplifier approach. The measurement technique developed is based on a PAR 129A lock-in, although a 124 lock-in was obtained on a trial basis from Princeton Applied Research to examine phase noise considerations in our error analysis studies.

Figure 2-10 shows the lock-in amplifier (LIA) impedance measuring system currently in use. The procedure for nulling phase throughout the electronics follows. To achieve minimum phase error one must null the smaller component of impedance, i.e., the capacitance. This is done by inserting a standard resistor in place of the device under test, and adjusting the phase dial until the LIA shows zero quadrature component, or capacitance. The quadrature channel will be nulled within the phase noise of the LIA (30 millidegrees for the 129A). The conduction channel, however, could have as much as 0.2 degrees phase error, due to the fact that the two channels are only guaranteed to be in quadrature within ± 0.2 degrees. This is negligible as long as $G > C$. At frequencies greater than 10 kHz available standard resistors have too much inductance to be considered ideal. In this case a standard capacitor must be used to null the system. This results in up to 0.2 degrees phase error, as well as additional error created by the common

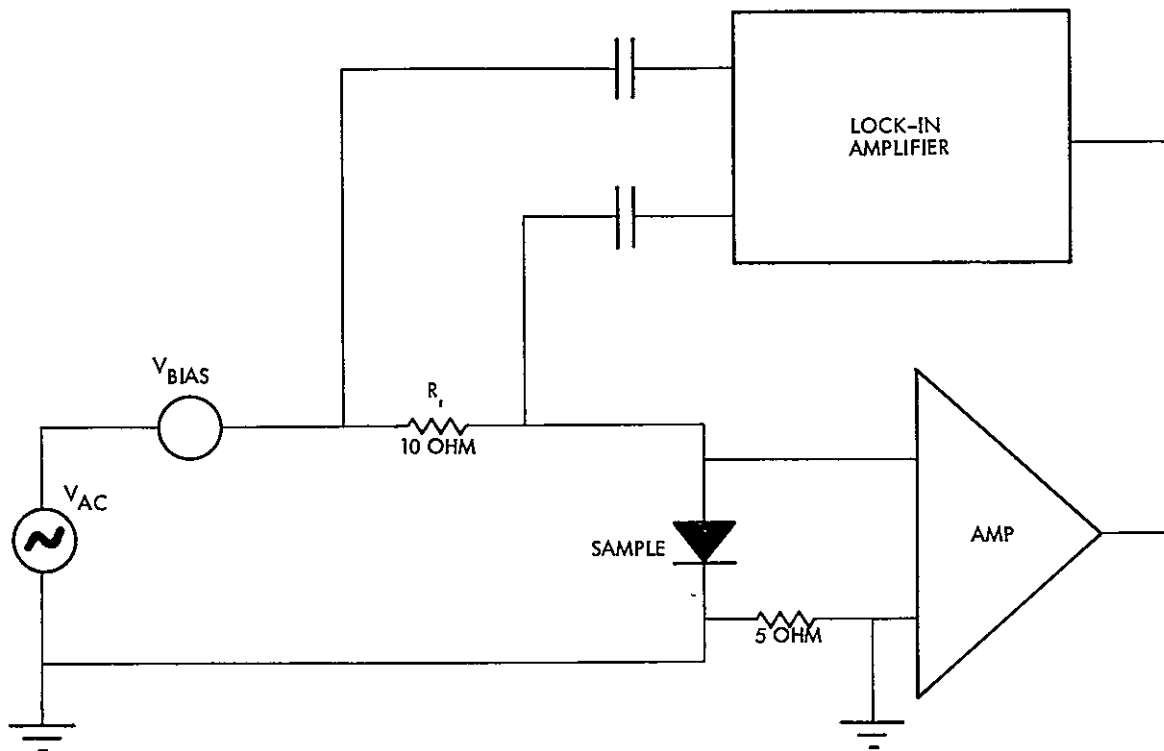


Figure 2-10. Lock-in Amplifier (LIA) Impedance Measuring System

mode voltage across R_j . When a capacitor is used to null the system, the common mode voltage is out of phase with the signal of interest and creates error if the common mode rejection ratio (CMRR) of the differential preamp is not sufficiently high. For the PAR 129A operated differentially, the CMRR is measured as 63db, causing an additional phase error of 0.06° . Therefore, the total phase error for the capacitive channel is estimated as 0.26 degrees above and 0.03 degrees below 10 kHz

In order to verify the accuracy of the LIA technique, several bridges have been considered. The Boonton Model 75C covers the frequency range of interest (5 kHz to 500 kHz), but is restricted to high impedance devices ($C < 1$ nF, $G < 1$ millimho). Use of this bridge would require a reduction in device area. Internal provision for biasing is provided, but current is limited to 10 milliamperes. Kar and Danlke also reported difficulty in using this bridge on baseline cells (Ref. 15). The General Radio 1621 can measure capacitance from 10^{-7} pF to 10 F, but conductance is limited to 1 millimho. The specified frequency range is 10 Hz to 100 kHz, but large errors in conductance occur at high frequency. Bias must be applied externally.

The General Radio 1608A was selected because this bridge can handle the impedance range of interest. The specified frequency range is 20 Hz to 20 kHz. However, by padding one of the bridge arms, useable data can be obtained up to 100 kHz. Internal switching provides several different bridges applicable at different impedances. At low bias, where capacitance dominates the device impedance, the " C_p " (parallel capacitance) or " C_s " (series capacitance) bridges can be used. In this case capacitance is measured directly and conduction is determined from the dissipation factor ($D = 1/\omega C_p R_p$). As device conduction increases, the G_p (parallel conduction) bridge becomes appropriate (Figure 2-11). Capacitance is determined from the device Q ($Q = \omega C_p / R_p$).

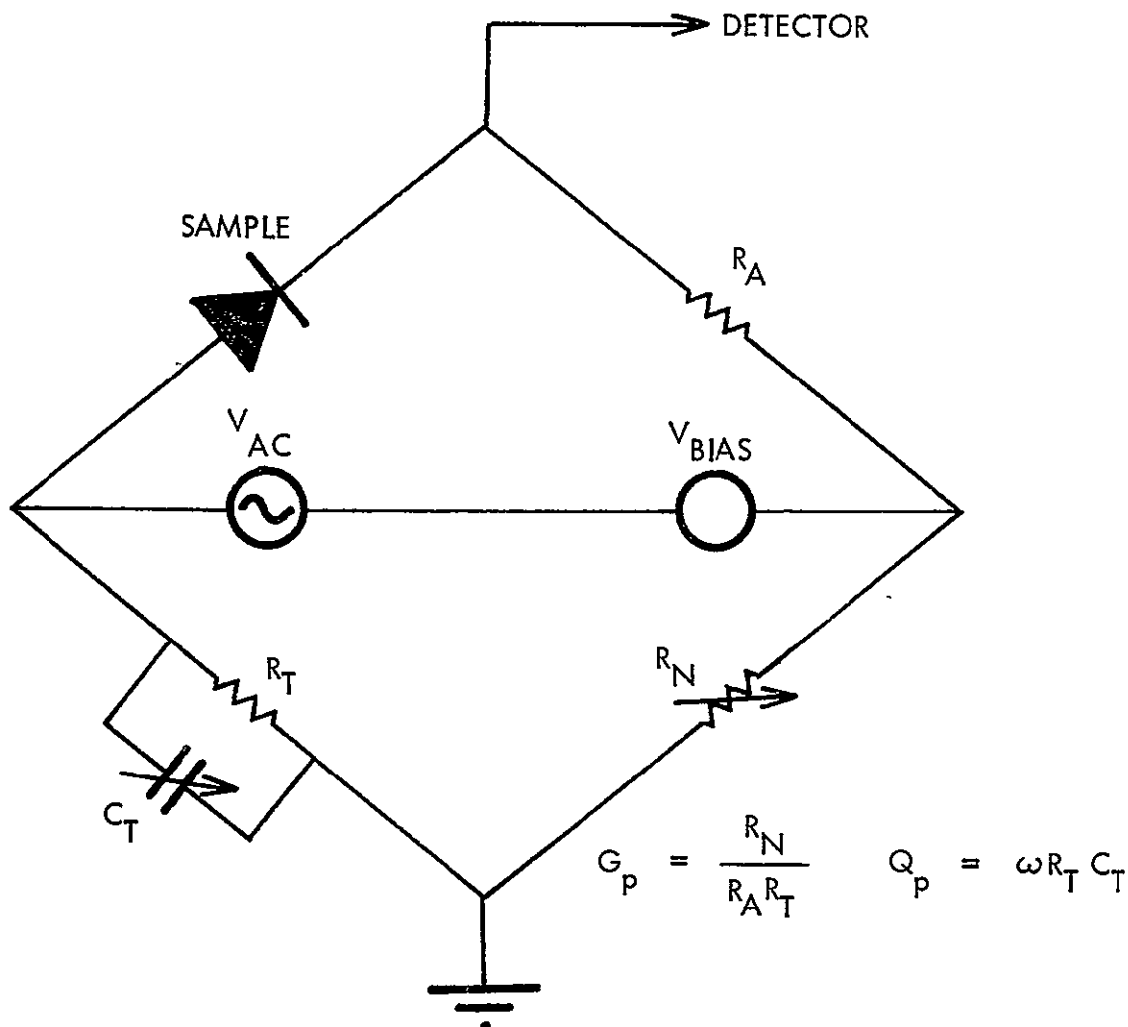


Figure 2-11. Bridge Circuit Used for Samples With Low Impedance

The majority of the data can be taken on the G_p bridge. This bridge measures G from 0.05 to 1.1 mhos., and Q from 0 to 1.2 at 1 kHz. The resolution of Q is ± 0.0005 . At higher frequencies, Q is scaled by a factor of $f(\text{kHz})/1 \text{ kHz}$. At 100 kHz the bridge will measure a Q from 0 to 100 with a resolution of ± 0.05 . Since the cells under forward bias are low Q structures, this resolution proves inadequate. The situation can be improved by paralleling R_T with another resistor. This can be done via front panel jacks. For a 1000 ohm external resistor the resolution of Q is improved by a factor of 7.67, yielding a resolution of ± 0.0066 at 100 kHz. and ± 0.00066 at 10 kHz.

The specified accuracy of the 1608A is given by:

$$\frac{\Delta C}{C} = [\pm 0.001 f^2(\text{kHz}) \pm 0.1D f(\text{kHz}) \pm 0.5D^2]\%$$

for the C_p and C_s bridge, and:

$$\frac{\Delta C}{C} = [\pm 0.002 f^2(\text{kHz}) \pm 0.000001 f^4(\text{kHz}) \pm 0.10]\%$$

for the G_p bridge. Errors in D and Q are small and do not increase with frequency. These equations predict that the bridge is useless above 20 kHz. In practice, with a 1000-ohm padding resistor, about $\pm 15\%$ error was found at 100 kHz. This required correction factors for residual bridge and cable inductance. The largest error was found when the unknown phase angle approached 45 degrees. Unfortunately, one must switch from the C_p or C_s bridge to the G_p bridge in this range. This could result in large discontinuities in capacitance and conductance. However, capacitive peaks tend to fall in the range of the G_p bridge, so that 1608A is useable for finding these at 100 kHz and estimating their magnitude.

The true value of the 1608A is that its error tends to be smallest where the lock-in amplifier has its largest possible error--when the impedance of the device under test approached pure conductance or pure capacitance. Under these circumstances the bridge has its highest accuracy. Since the lock-in measures ωC , the capacitive or quadrature component is smallest at low frequency (and hence, the possible error largest) where the 1680A is most accurate. For the majority of measurements, the lock-in has superior accuracy and is easier to use.

The lock-in can also be used as an external detector for the bridge. This eliminates errors caused by 60-cycle line noise and harmonics of the signal frequency. Standard detectors only indicate a minimum in the magnitude of an applied signal. With a lock-in, one can be assured that both the real and imaginary components of a signal are nulled.

3. Analysis and Theoretical Modeling

Considerable effort has also been spent on developing a theoretical model for interpreting C_p and G_p data. Although a theoretical model had been proposed elsewhere (Ref. 15), the analysis developed here showed that, for high conductance M-I-S structures, minority band effects cannot be neglected and do significantly affect the interpretation.

Theoretical modeling has also been done showing the effect of tunneling resistance to minority carries on C_p and G_p data. It has also been shown theoretically that surface states alone cannot give a diode ideality factor $n > 1$ at low bias because of surface recombination currents.

To date the samples examined have been native oxide devices (GaAs with some inadvertent interfacial film and Au metallization) and O_2 /water vapor oxide devices. These surfaces are metallized with Au forming a M-I-S structure. Figure 2-12 shows I-V data for a virgin GaAs chip (II-1) which has been used to fabricate a water vapor oxide M-I-S structure. The dark I-V yields an n factor of about 1.2, being larger at lower biasing. Localized state density was found to be $\sim 2 \times 10^{11} (\text{eV}^{-1} \text{cm}^{-2})$. If they were the cause of the n factor, the n factor would be given by the approximate expression*:

$$n \simeq 1 + \frac{C_n + C_s}{C_i},$$

which comes from

(2-5)

$$\Delta V = \frac{C_n + C_s}{C_i} \Delta V_s + \Delta V_{s'},$$

where C_n is the capacitance due to the depletion layer.

The interfacial capacitance (C_i) can be approximated by assuming a 20Å thickness and a dielectric constant ϵ . This gives

$$C_i \simeq 8.9 \epsilon \text{ A} \simeq 100 \epsilon (\text{nF}).$$

(2-6)

Assuming ϵ is unity, this yields an n factor of about 1.04 if there were no localized states. Following this approximation and using the data of Figure 2-12 shows that the measured localized states density gives an n of ~ 1.11 for this device. Clearly this predicted low n value (and the actual relatively low n value) do not explain the enhanced light I-V performance. The enhanced V_{oc} is also due to a lower reverse saturation current as stated in Section II.B.

*Appropriate because n is defined by $n \equiv V/V_s$ not dV/dV_s .

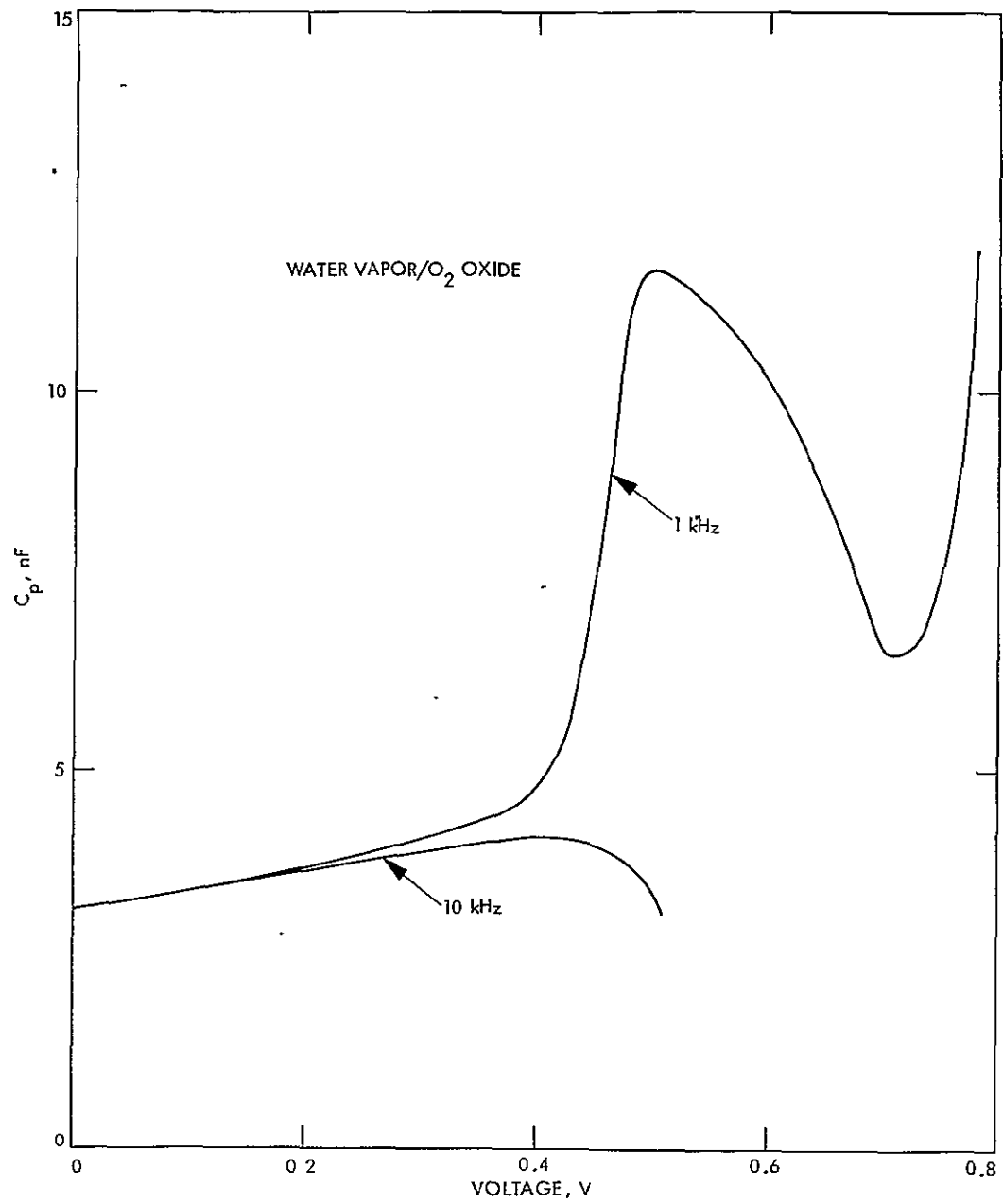


Figure 2-12. C-V Data for Oxide-GaAs Interface at Two Frequencies

Figure 2-13 shows the corresponding data for the same chip after it was recycled. Here the only oxide present is that which inadvertently occurs. As expected, light I-V performance is not as good as that of the previous structure on the virgin chip in that V_{oc} is about 460 mV. Also the n factor is about 1.4 too high for a baseline cell. Data from Figure 2-13 yield a localized state density of $\sim 10^{12}(\text{eV}^{-1}\text{cm}^{-2})$. Eq. (2-5) and (2-6) predict an n factor of ~ 1.4 . This agreement with the dark I-V value is quite fortuitous; however, the agreement in trend is apparent. This device gives poor photovoltaic performance because of a larger saturation current. The role of recycling is not clear at this point.

The decreasing high frequency capacitance seen in the water vapor oxide shown here has been seen in other similar oxides. It is believed to be caused by tunneling resistance to minority carriers (holes); this point is being examined. Also, the larger n values seen at the lower biases in the dark I-V data presented here seem typical. This does not seem to be due to localized state charge storage, but rather, is probably an additional current channel. This is also being further explored.

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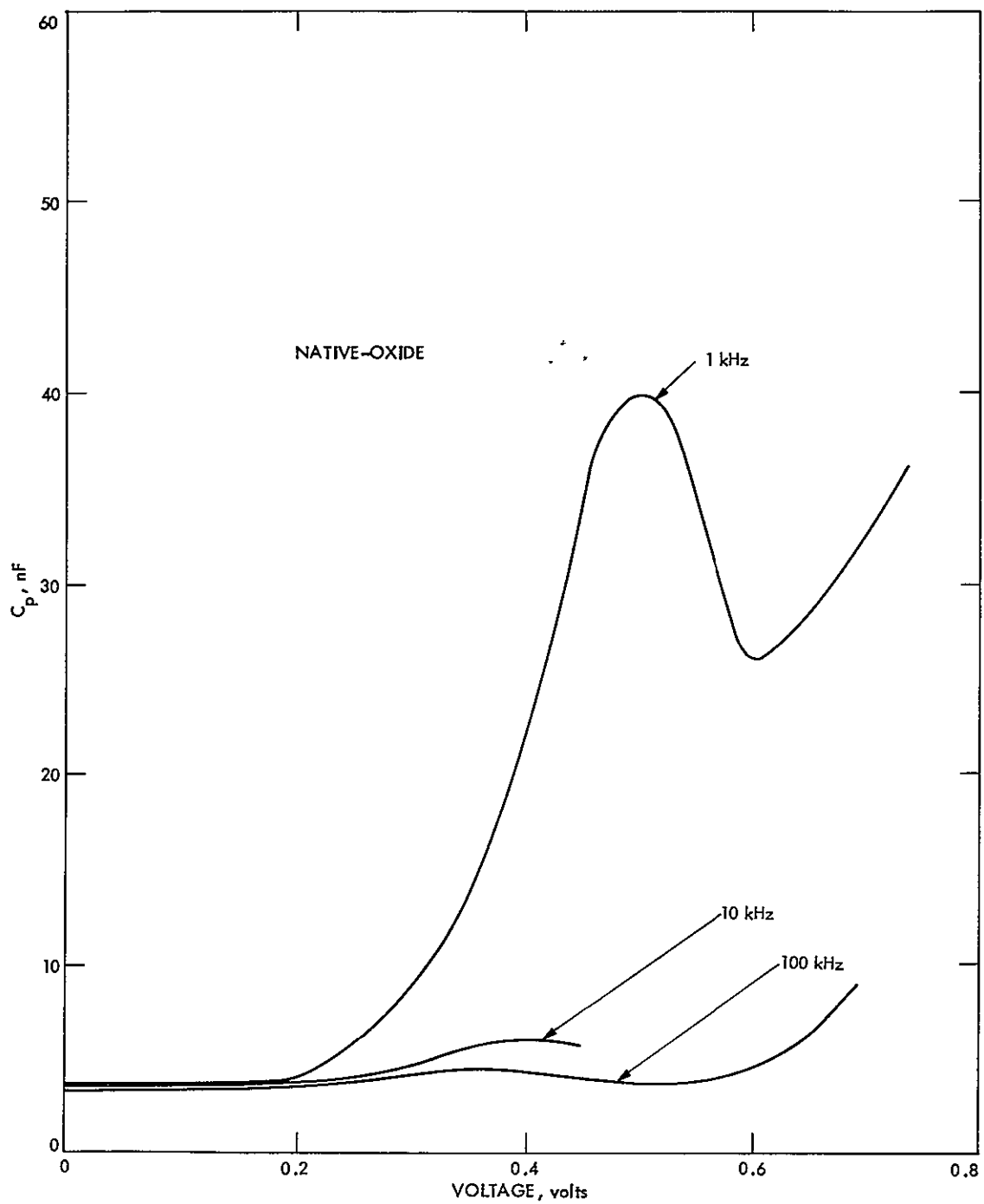


Figure 2-13. C-V Data for Native Oxide-GaAs Interface at Three Frequencies

SECTION III

THICK-WAFER POLYCRYSTALLINE AMOS SOLAR CELLS

A. SCANNING ELECTRON MICROSCOPE STUDIES

Schottky barrier solar cells were fabricated on sliced wafers of bulk polycrystalline GaAs in order to study the role, if any, of grain boundaries on the cell properties. This phase would provide intermediate results for relatively large grains subsequent to the availability of thin-film GaAs on recrystallized Ge.

One would anticipate that the short-circuit current output of these wafers would be primarily dependent on the quality of the GaAs within the grain, and that the effect of the grain boundary would be small for minimum grain sizes of $\geq 10 \mu\text{m}$. For example, if the minority carrier diffusion length was $1 \mu\text{m}$ within $10\text{-}\mu\text{m}$ grains, simple geometrical arguments would say that about 80% of the carriers would be collected as compared to single crystalline material assuming that about one-half of the carriers generated within $1 \mu\text{m}$ from a grain boundary recombine at the boundary.* But even more carriers will be collected considering the fact that the built-in electric field of the SB extends several tenths of a micrometer in the bulk for the operating bias of about 0.7 volts at the maximum power point, and the fact that over half of the photons are absorbed within the first micrometer of GaAs.

The values of open-circuit voltage for polycrystalline SB solar cells are less predictable. Even for the baseline SB cell, V_{OC} will depend on variations in barrier height within the grains due to the crystallographic orientation randomness, and at the grain boundary due possibly to enhanced thermionic-field emission (increased carrier concentration) or to shifts in Fermi level pinning (disrupted bonds). The situation is even more complex for the case of SB cells with the interfacial oxide layer (AMOS). Some preliminary results are presented in the following.

Sliced wafers of polycrystalline GaAs were purchased from Crystal Specialties, Inc. of Monrovia, California. The wafers were cut to shape, lapped, but not polished, in order to reveal the polycrystalline structures by differences in light reflectivity. Figure 3-1 is an optical photograph of a sliced polycrystalline GaAs wafer. Four circular thin gold films had been deposited to indicate on the photograph the location of the eventual devices. A Au/Ge/Ni ohmic back contact was then applied to the wafer, which was then mounted to a tantalum sheet backing with conductive epoxy for improved handling. Chemical polishing and etching the polycrystalline wafer removed mechanical damage caused by lapping. Four baseline SB cells were fabricated using gold metallization.

*The assumption is also made that the film thickness is at least $3 \mu\text{m}$ -- sufficient to absorb nearly all photons and to have negligible back contact effects.

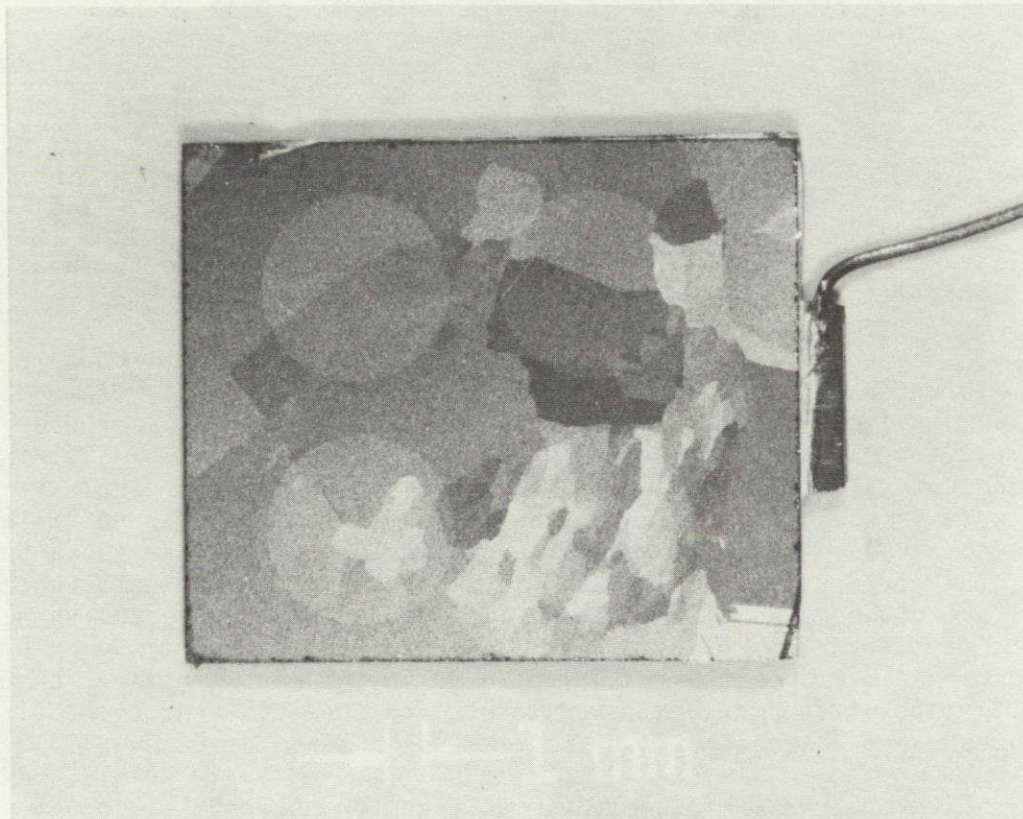


Figure 3-1. Optical Photograph of a Sliced, Lapped but Unpolished Polycrystalline GaAs Wafer Coated With Four Ultra-Thin Films of Evaporated Gold

Although the true nature of the polycrystallinity was not brought out by the optical photograph (Figure 3-1), EBIC-mode SEM pictures indicate the influence of grain boundaries and defects on charge carrier collection at the surface. In the EBIC mode, induced beam current due to minority carriers collected at the SB from electron-hole pairs generated by the scanning primary electron beam is amplified, contrast-enhanced, and displayed on a cathode ray tube. Regions of the semiconductor where recombination of the minority carriers are greater, such as at grain boundaries, are clearly indicated. Figure 3-2 is an EBIC-mode photograph of a SB cell made in the same region as the 5-mm circular disk shown in the lower right-hand side of Figure 3-1.

Considerably more structure is seen in Figure 3-2 than is evident in Figure 3-1. The grain boundary structure can easily be distinguished from surface scratches. The sizes of the grains range from 100 to 500 micrometers. In order to prove that the observed structures were not

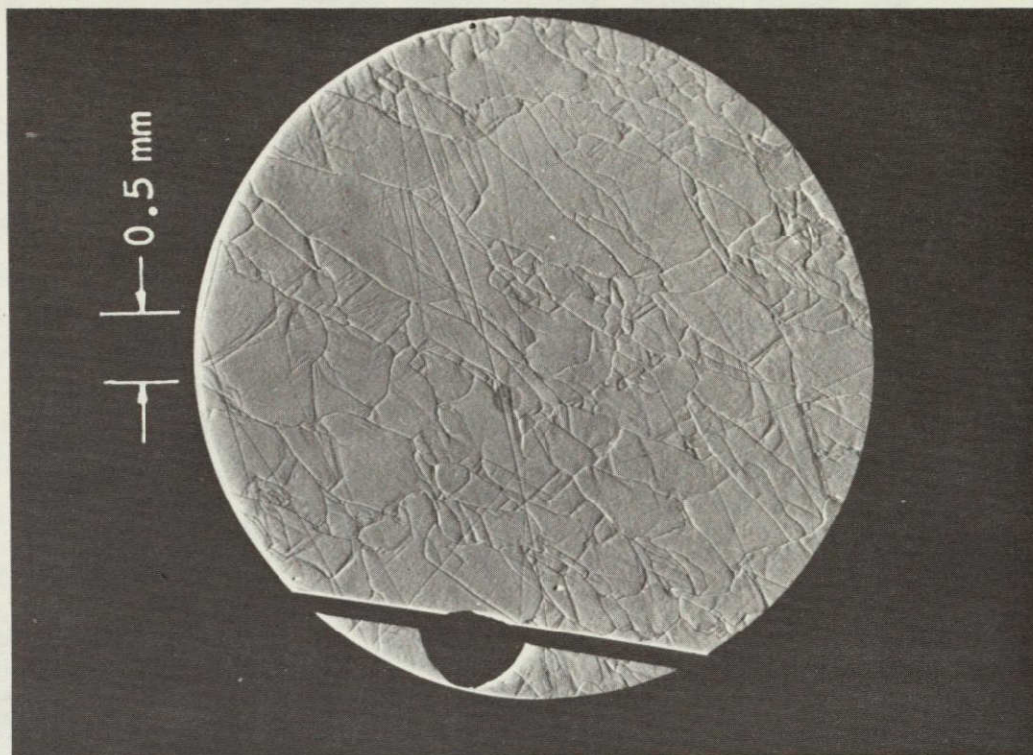


Figure 3-2. EBIC Picture of Sample Area in Lower Right Hand Portion of Wafer in Figure 3-1

introduced by artifacts, an EBIC-mode photograph (not shown) was also taken of a sample cell made on a single crystal GaAs wafer for comparison. As expected, that photograph was featureless.

Another useful feature of EBIC-mode SEM involves displaying the amplitude of the EBIC signal along a single scan line as a function of spatial displacement. Relative quantitative information can then be obtained about localized response. By correlating the EBIC-mode photograph and the single-line scan signal, the influence of grain boundaries or defects can be determined. This feature is demonstrated in Figure 3-3, where the EBIC signal is shown in the upper portion of the photograph and the light trace indicates the location of the single scan line on the sample surface. The reference, corresponding to zero signal, is clearly indicated in the upper far right of the figure. It is associated with the non-responsive area on the base GaAs substrate not metallized with gold. The signal level along the

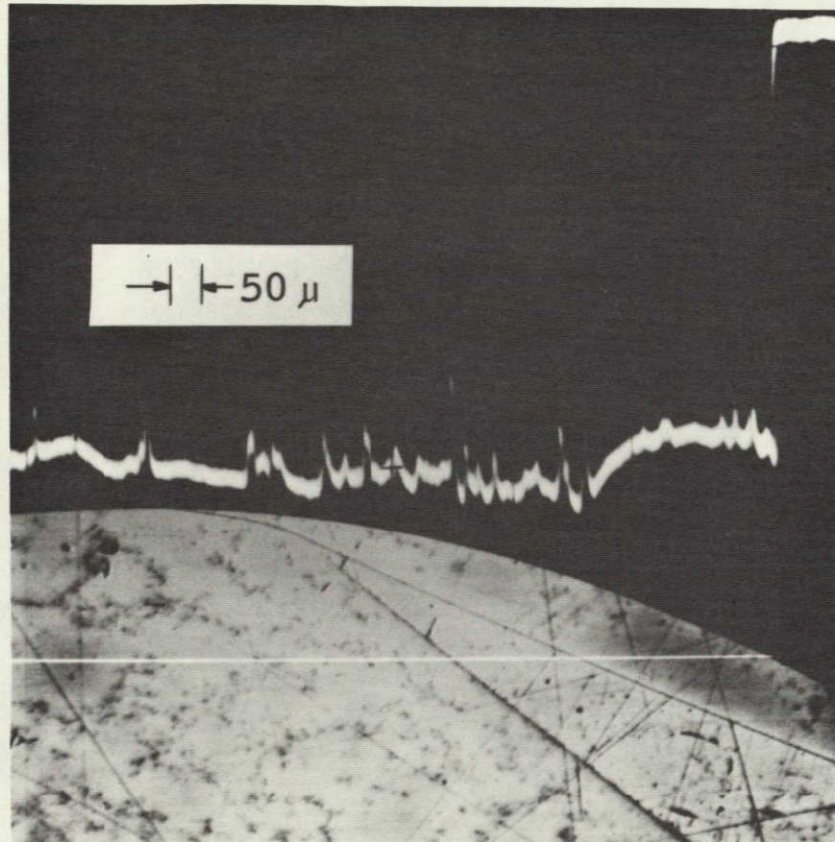


Figure 3-3. EBIC Picture and Amplitude-Modulated Signal From a Single Line Scan Across a Schottky Barrier Made on Polycrystalline GaAs

sample cell is reduced by up to 20% when the primary electron beam passes over either a grain boundary, defect structures, or a scratch line. The dark specks are probably caused by localized defects such as inclusions, dislocations, etc. The scratch lines were caused by inadvertent particulate matter embedded in the polishing pad. Since 10-KeV primary electron beam was used, the penetration depth of the electrons is about $0.6\text{ }\mu\text{m}$ - comparable to the absorption depth of solar radiation. Therefore, the degradation of current output shown in the EBIC signal should be comparable to the actual photovoltaic response.

The width of the peaks gives a measure of the region which is relatively non-responsive. This region should be approximately equal to the physical width of the disrupted area plus an additional width dependent on the minority carrier diffusion length, the depth of the depletion region, and the depth distribution of the generated minority carriers. The minority carrier diffusion length of this polycrystalline

material is on the order of one micron based on the measured short-circuit current with simulated AM1 sunlight. Figure 3-4 is a magnified picture of one portion of the sample in Figure 3-3. The average regions of reduced output are seen to be approximately five micrometers in width. Since the maximum reduction of induced current due to grain boundaries, etc., appears to be 20% less than what is observed in the normal regions, the total current reduction in a polycrystalline GaAs SB solar cell, assuming 100- μm square grains with 5- μm wide boundaries, would be about 2% less than the current from a single crystal of GaAs with the same material parameters as within each grain. Indeed, SB cells made in regions where only a few grain boundaries existed showed no detectable differences in short-circuit current output from that in cells fabricated in regions where the grain sizes were smaller, such as shown in Figure 3-2.

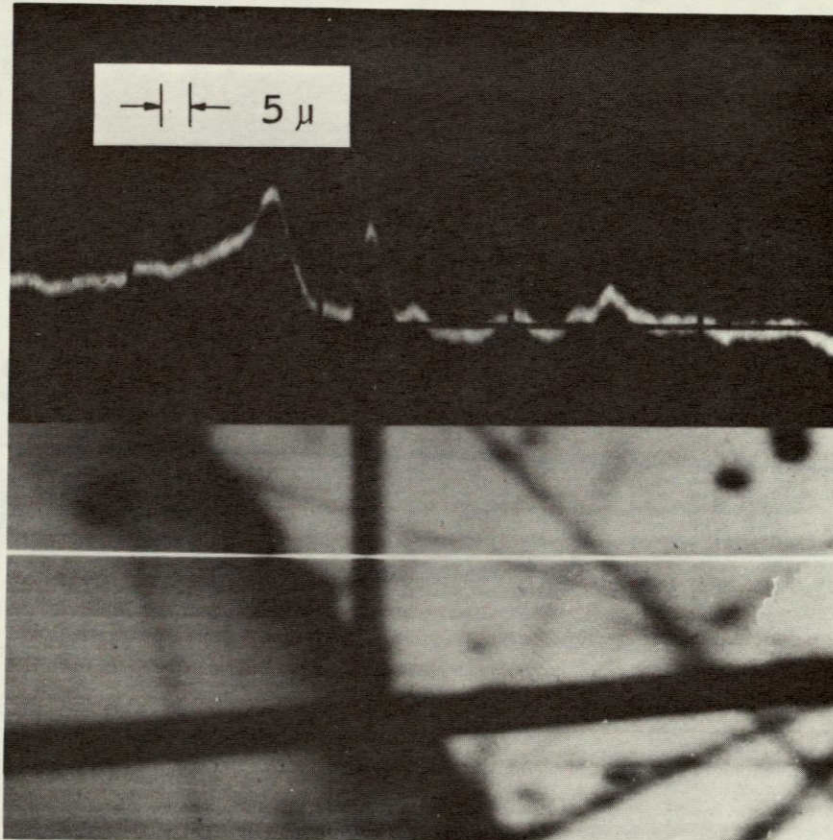


Figure 3-4. EBIC Picture of a Portion Shown in Figure 3-3, but Magnified Ten Times

B. POLYCRYSTALLINE SOLAR CELL CHARACTERISTICS

The same polycrystalline substrates used for the SEM studies were analyzed for their photovoltaic characteristics in both the baseline and AMOS configurations using the older chemical etching procedure. From capacitance-voltage measurements of the baseline cell, the doping concentration was found to vary between 1.5 and $3 \times 10^{17} \text{ cm}^{-3}$ across the wafer surface. This doping concentration is in the range where additional diode current due to tunneling occurs. The barrier height measured by photoresponse for the metal consequently showed barrier lowering with values for the barrier height of $0.87 \pm 0.02 \text{ eV}$ as compared to $0.90 - 0.97 \text{ eV}$ for lighter-doped single crystals (100, 111 and $\bar{1}\bar{1}\bar{1}$ orientations). The reduction in barrier height was also confirmed by the lower V_{oc} value (430 mV) for a baseline cell made on a sliced polycrystalline substrate (curve 1 of Figure 3-5). A V_{oc} of $0.45 - 0.52 \text{ V}$ is observed for typical baseline cells of single crystals with different orientations. Baseline cells made on different wafers cut from the

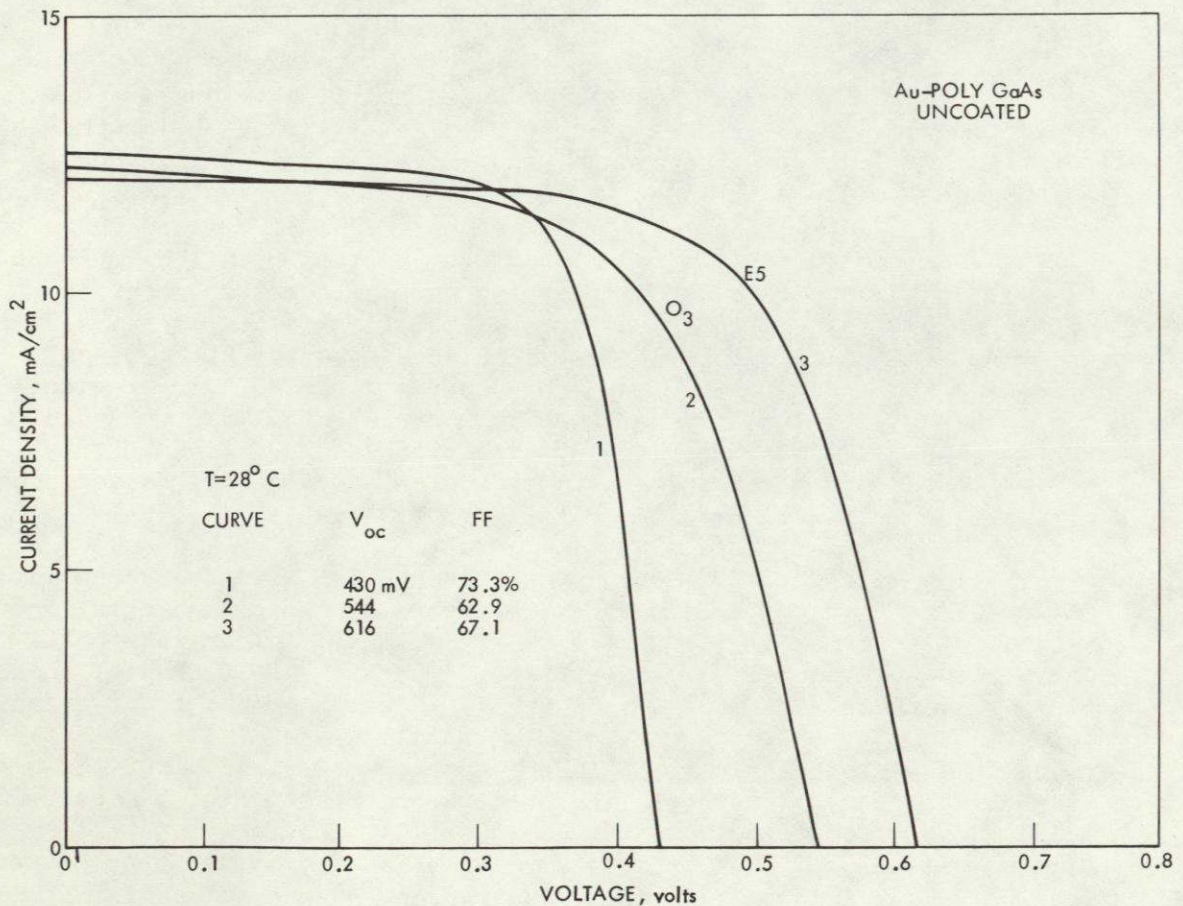


Figure 3-5. Light I-V Characteristics for 60Å Gold on Bulk Polycrystalline GaAs With $1-3 \times 10^{17} \text{ cm}^{-3}$ Doping

same polycrystalline boule gave similar V_{oc} values within 5%. This suggests that the relative number of grain boundaries makes little difference on V_{oc} , at least for the scale of grain sizes in our sliced polycrystalline material (order of 100 micrometers).

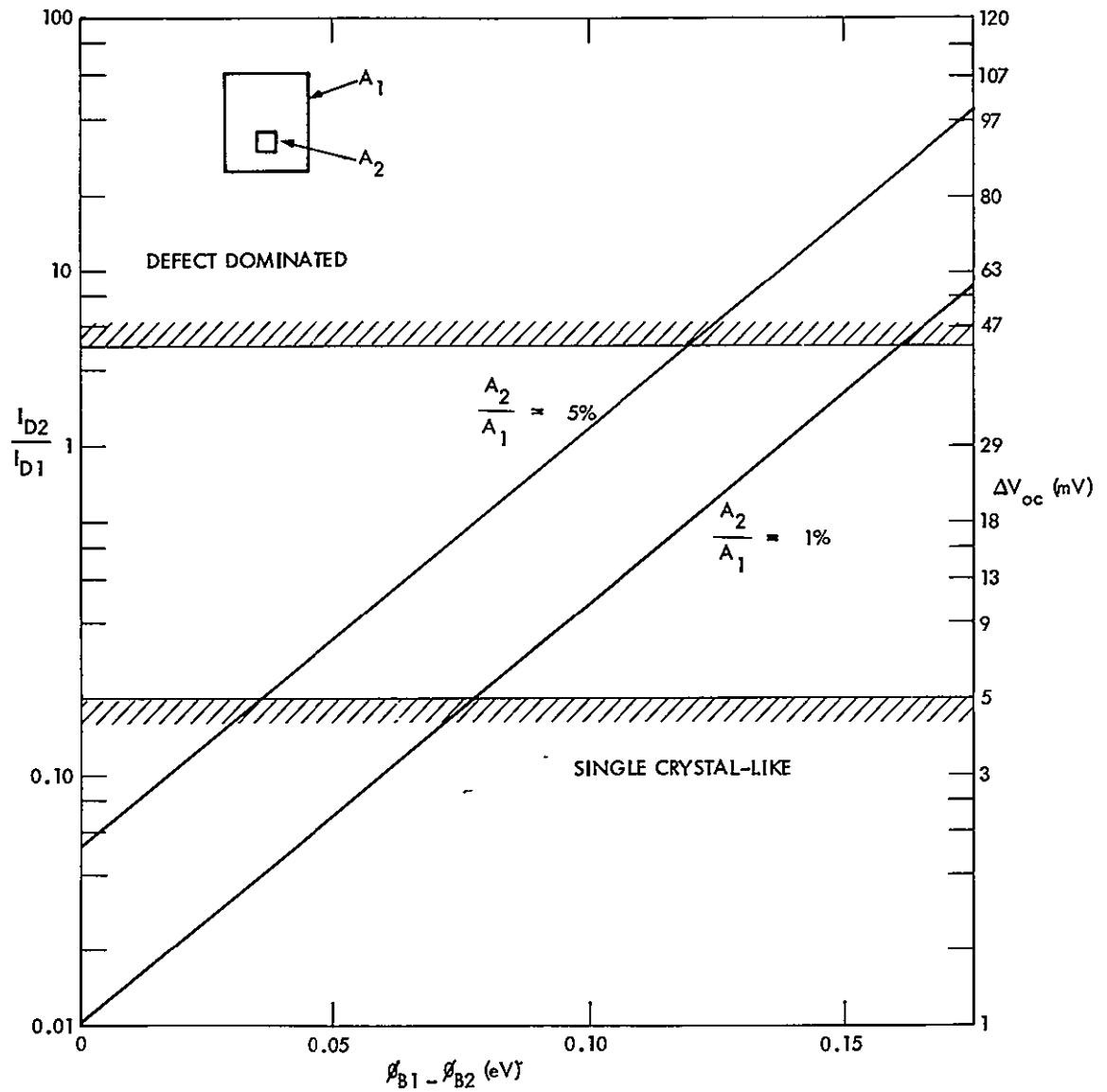
The observed short-circuit current (I_{sc}) is about 20% lower than that of single crystal cells with carrier concentration in the 10^{15} - 10^{16} cm^{-3} range. The 20% reduction in I_{sc} is due to a shorter minority carrier diffusion length and a narrower depletion region rather than due to the polycrystallinity per se. This will be shown below when results are discussed for cells made on CVD layers grown on the same substrates.

Next, AMOS technology was applied to the sliced poly-GaAs wafer with no attempt made to optimize the oxidation process. Values of V_{oc} of 0.55 and 0.62 V were obtained for samples oxidized by the ozone and E5 process, respectively, as shown by curves 2 and 3 in Figure 3-5. The V_{oc} value is lower by about 100 mV than that obtained for single crystal (100) GaAs. The smaller V_{oc} may be partially due to the high doping concentration in the polycrystalline substrate as well as the fact that the enhancement in voltage with oxidation is different for different crystalline orientations.

In addition to the reasons mentioned above, the lower value of V_{oc} could also be due to the grain boundaries. The barrier height may be modified by a shift in the pinned Fermi level at the surface due to changes in surface state density at the grain boundaries. If some such mechanism did act to change the barrier height locally, the change in V_{oc} can be calculated as a function of the barrier height difference. Figure 3-6 shows such a calculation for two different area ratios assuming that the empirical n factor is the same in both areas. In the example of the sliced poly-GaAs wafer discussed above with 100- μm average sized grains and 5 μm -wide reduced voltage boundary regions, the area ratio is 10%. If one were to postulate that the enhanced barrier heights of 1.05 eV were obtained within the grain and only 0.9 eV in the boundary regions, the calculations show that a lowering of 90 mV in V_{oc} would occur.

Sliced polycrystalline substrates were then given to Rockwell International for growth of epitaxial layers by the organo-metallic CVD method.* Baseline SB solar cells were fabricated on a highly polycrystalline region of these substrates. The light I-V curve of such a baseline SB cell (Figure 3-7, curve 1) showed that the short-circuit current was even slightly more than we usually measure for cells fabricated on CVD single crystal GaAs from Applied Materials, Inc. grown by the halide transport method. The doping concentration of the poly-GaAs measured by capacitance-voltage was $1\text{-}2 \times 10^{16} \text{ cm}^{-3}$, whereas the commercial single crystal GaAs we have used in this program has been between 2×10^{15} and $4 \times 10^{16} \text{ cm}^{-3}$. Thus, the larger current output is not due to an increase in depletion width, but rather, due to a larger minority

*The assistance of Drs. R. Ruth and D. Dapkus was appreciated.



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Figure 3-6. Influence of Defect-Modified Barrier Heights on V_{OC} , Representing the Sum Total of Such Areas by A_2 and the Unaffected Areas by A_1

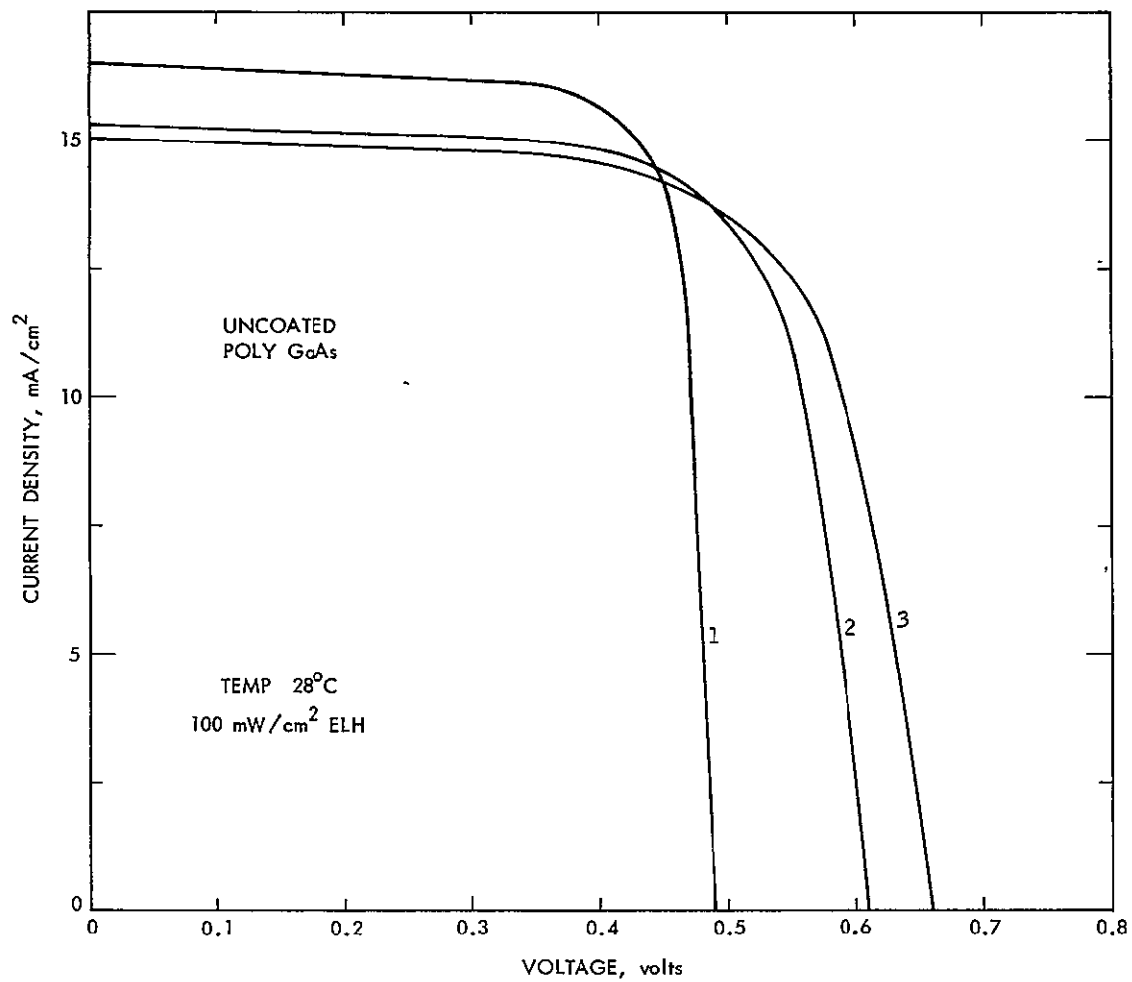


Figure 3-7. Light I-V Characteristic of Baseline (Curves) and AMOS Solar Cells Made on Wafer Used in Figure 3-5 but With an Epitaxial GaAs Layer Grown by Organo-Metallic CVD ($n = 1.1 \times 10^{16} \text{ cm}^{-3}$)

carrier diffusion length. The high short-circuit current also verifies our finding in the SEM-EBIC study that the influence of grain boundaries on current output is insignificant when the average grain size of the polycrystalline substrate is 100 μm or larger.

The value of V_{OC} (Fig. 3-7, curve 1) is 0.49 volt - comparable with the value of a typical single crystal baseline SB solar cell. This result demonstrates that the grain boundaries have little effect on the V_{OC} value for baseline cells.

The AMOS technology described earlier was then applied to the same sample. Figure 3-7 shows light I-V curves for two samples which had the oxide grown by an oxygen gas discharge (curve 2) and by ozone (curve 3). The O_2 pressure was 200 microns and exposure time 1 minute for gas discharge case. The average oxide thickness in each case was about 30Å as measured by ellipsometry. While the current output of the AMOS cell made on poly-GaAs with CVD layer on top (15 ma/cm^2 uncoated) is larger than that of an AMOS cell made directly on the bulk-grown poly-GaAs (12.5 ma/cm^2 uncoated), the value of V_{OC} is only slightly higher. Moreover, the V_{OC} values of the AMOS poly wafers are about 30 - 80 mV lower in comparison with (100) single crystal cells for various oxidation process. This implies either that the random crystallographic orientation of individual grains are responsible for the lower V_{OC} value, and/or that the AMOS processing has little or no effect in those regions influenced by the grain boundary. Since the oxidation processes for the poly-GaAs has not been optimized, further improvement in V_{OC} of the AMOS poly-GaAs cell is expected.

SECTION IV

THIN-FILM POLYCRYSTALLINE AMOS SOLAR CELLS

A. APPROACH

Three major factors that need to be considered when evaluating the potential of solar cells for large-scale terrestrial applications are: (1) efficiency or power output per unit area for a defined illumination, (2) availability of the materials, and (3) economic costs. There is a clear trade-off between the array efficiency and its associated costs. A first generation thin-film GaAs structure which promises relatively high efficiency is shown in Figure 4-1. This structure is similar to the device shown in Figure 1-1 with the major (and crucial) difference being the replacement of the single crystal GaAs with polycrystalline GaAs chemically vapor deposited on a recrystallized film of germanium (Ge). The latter film is deposited on a low-cost conducting or metallized insulating substrate.

A general rule-of-thumb in thin-film photovoltaics is that the crystallite size should be at least as large in diameter as the thickness of the film. This is to minimize the effect of grain boundaries parallel to the substrate that would limit the minority carrier flow toward the collection plane. Larger crystallites are even more desirable, of course, since the total number of grain boundaries is smaller, thereby reducing the number of minority carriers recombining at such boundaries during the course of their diffusion toward the collection plane. This is particularly true for materials with long diffusion lengths such as Si. Also, reducing the number of grain boundaries by increasing the grain size will lessen the problems that arise when forming potential barriers in polycrystalline films. (See Section III).

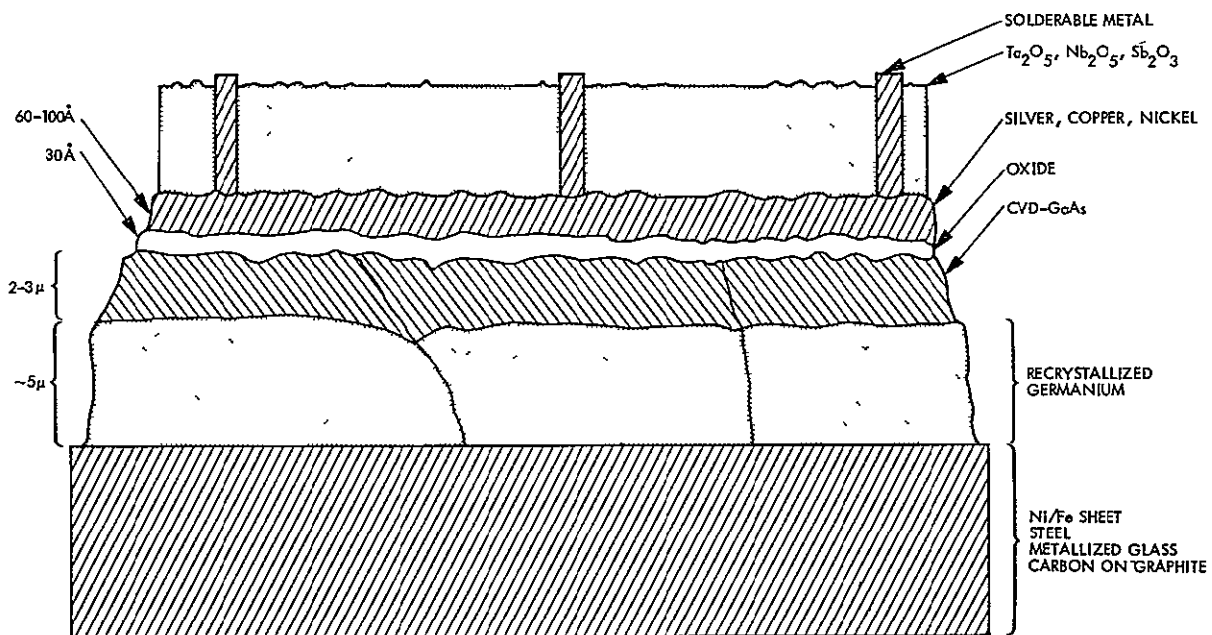


Figure 4-1. Thin Film AMOS Solar Cell (not to scale)

In a direct-gap semiconductor, such as GaAs, most of the photons are absorbed in the first 2 or 3 microns. This and the fact that minority carrier diffusion lengths in GaAs are only a few microns at best, and more likely, about one micron or less in thin films, implies that output current densities can be relatively high in GaAs films with grain sizes of some tens of microns if the deposition process produces GaAs with impurity characteristics similar to those now obtained in epi-layers. Further increases in the grain size are still highly desirable, of course, for the reasons mentioned above.

The purpose of the Ge layer in the present approach is to provide for a more ordered larger grain GaAs film. Ge was chosen as the inter-layer because it has a very close match to GaAs in lattice parameter and in thermal coefficient of expansion (Ref. 16). Even at the growth temperature of GaAs ($\sim 700^\circ\text{C}$), the mismatch in lattice parameter is only about 0.1% and less than that at room temperature. Normally, evaporated films have grain sizes with dimensions of submicrons or microns. It has been shown by several laboratories that evaporated Ge films can be recrystallized to millimeter-size crystallites for relatively small areas (Refs. 17-20). This early work was not pursued because of the lack of interest in Ge for device application. The approach used on this program to recrystallize large areas economically is discussed below.

The GaAs layers grown by CVD (chemical vapor deposition) could become doped with Ge by transport of Ge which has entered the gas stream from etching action of the substrate by HCl vapor in halide growth systems or by diffusion through the interface. The first effect is non-existent in CVD systems using organo-metallic sources and would be reduced in systems using HCl vapor since thin films of Ge on substrates would not have exposed sides or back such as a single crystal wafer would.

Both of the semiconducting layers need to be doped for the same polarity so as to avoid a reverse-biased p/n heterojunction at the interface. The autodoping by diffusion of Ge through the interface has been found to be exponentially dependent on the distance from the interface with no detectable amounts beyond 3 micrometers (Ref. 21).

Another aspect of small crystallite films that usually prevents the fabrication of useful devices is the poor quality of diffused p-n junctions. The diode characteristics of diffused junctions in films invariably show excessive amounts of leakage current and space-charge recombination current leading to low voltages and fill factors. The shunting problems apparently arise from enhanced shallow level impurity diffusion along grain boundaries toward the substrate, particularly that of the dopant species. It has long been felt that these problems should be circumvented to some degree by the use of a metal-semiconductor or Schottky barrier contact, as discussed in Section III.

One problem to expect for MS contacts on polycrystalline films is a higher sheet resistance of the metal film for a given thickness as compared to single crystal SB solar cells because of the expected "roughness" of the polycrystalline film. Undoubtedly, the use of

multiple evaporation sources (probably four in a production mode) will allow for thinner metal films for a given sheet resistance because of an expected lessening of microscopic shadowing effects. Current single crystal cells on polished surfaces have a sheet resistance of about 50 ohms/sq for 60Å of gold. Depending on the ultimate grid configuration, a much higher value can be tolerated--certainly several hundred ohms/sq. As stated earlier, metals other than gold will be investigated in the future for improved stability at high temperatures and for economy.

Preliminary work has shown that both GaAs and Ge wet tungsten quite well. In fact, GaAs films were reported to have highly oriented grains when evaporated on tungsten (Refs. 22, 23) as compared to other metallic substrates. Pure tungsten substrates are far too expensive for solar cell application; however, silicon steel, Ni/Fe alloy graphite, or appropriate insulating substrates coated with CVD-deposited tungsten may provide good substrate material because of their reasonably good thermal expansion match with Ge or GaAs (Figure 4-2).

B. MATERIAL AVAILABILITY

Assuming a film thickness of 2 μm for GaAs and 5 μm for Ge, 80% utilization of the material, and 15% efficiency (a value that may be possible with one version of the thin-film AMOS solar cell), 500 MW of peak power or $3.3 \times 10^6 \text{ m}^2$ of cell area would require 24.7-23.9-, and 112- metric tons (MT) of Ga, As, and Ge, respectively. Annual production of ten to one hundred times these quantities may be desirable depending on the success of alternate energy sources that may be developed.

The present world production of arsenic, which is approximately 52,000-MT per year, and identified U.S. resources of 1.2×10^6 -MT (Ref. 24) are more than ample. The U.S. production of about 20,000 MT per year (Ref. 25) is a byproduct of copper and lead production and is primarily used in the agricultural industry for pesticides.

Estimates of available Ge in zinc ores suggest that a several fold increase in annual production to more than 600 MT is feasible (Ref. 26). A considerably larger amount may become available should coal gasification become widely used.

The availability of Ga (at a reasonable cost) is less certain. Present production--primarily as byproduct of the Bayer process for producing alumina from bauxite--is demand limited. If all of the Ga were extracted during the production of aluminum, well over 1000 MT per year would be available in the U.S. at the present rate of Al production. However, not all of the Ga can be extracted with reasonable cost. A recent study by ALCOA (Ref. 26) estimated the potential production of Ga from bauxite sources used in domestic Al production. Figure 4-3 shows the annual U.S. Ga potential as a function of the Ga concentration at which the plant is operated. The latter function is a measure of the economics since a lower concentration requires a larger volume to process.

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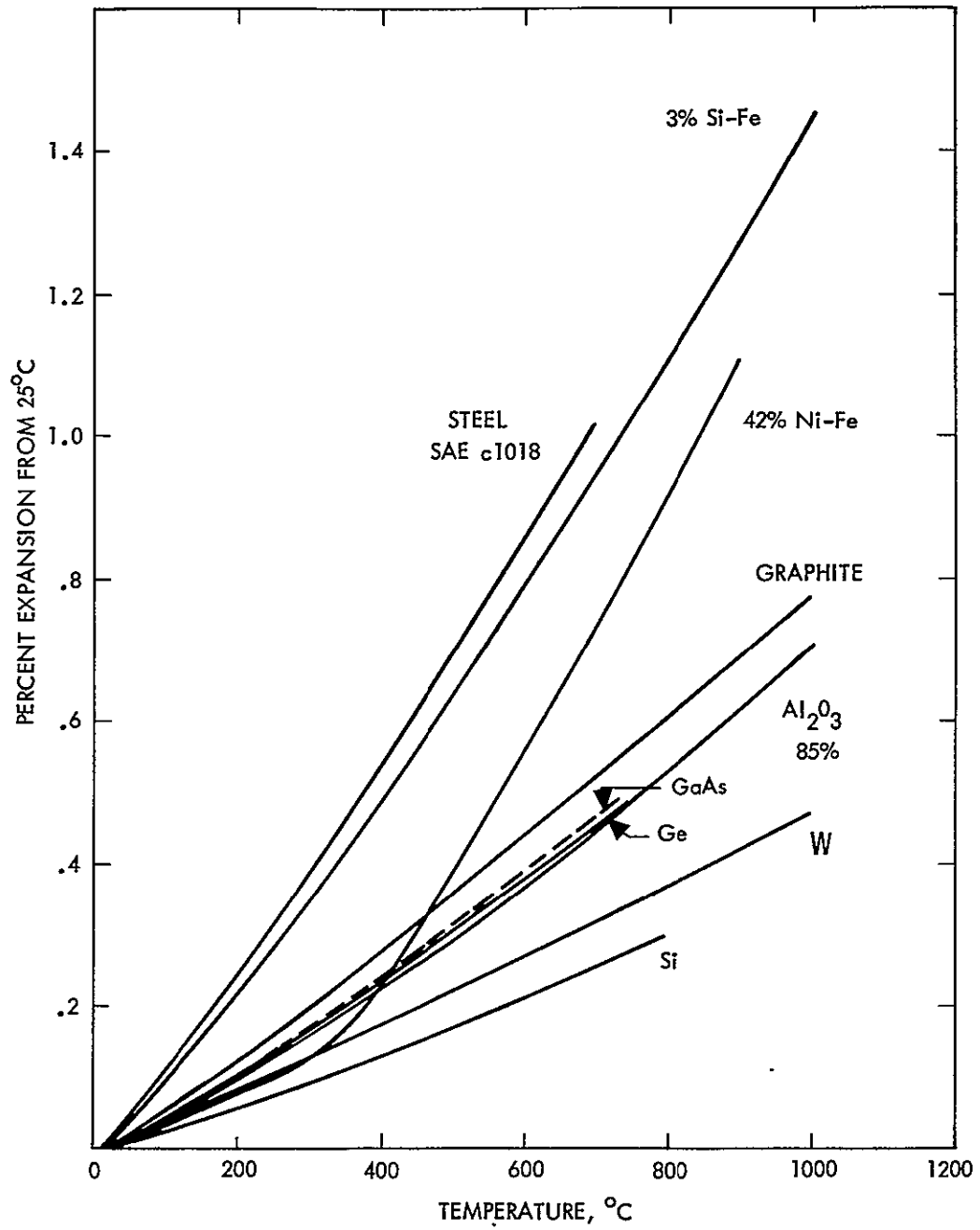


Figure 4-2. Percent Expansion for Selected Materials

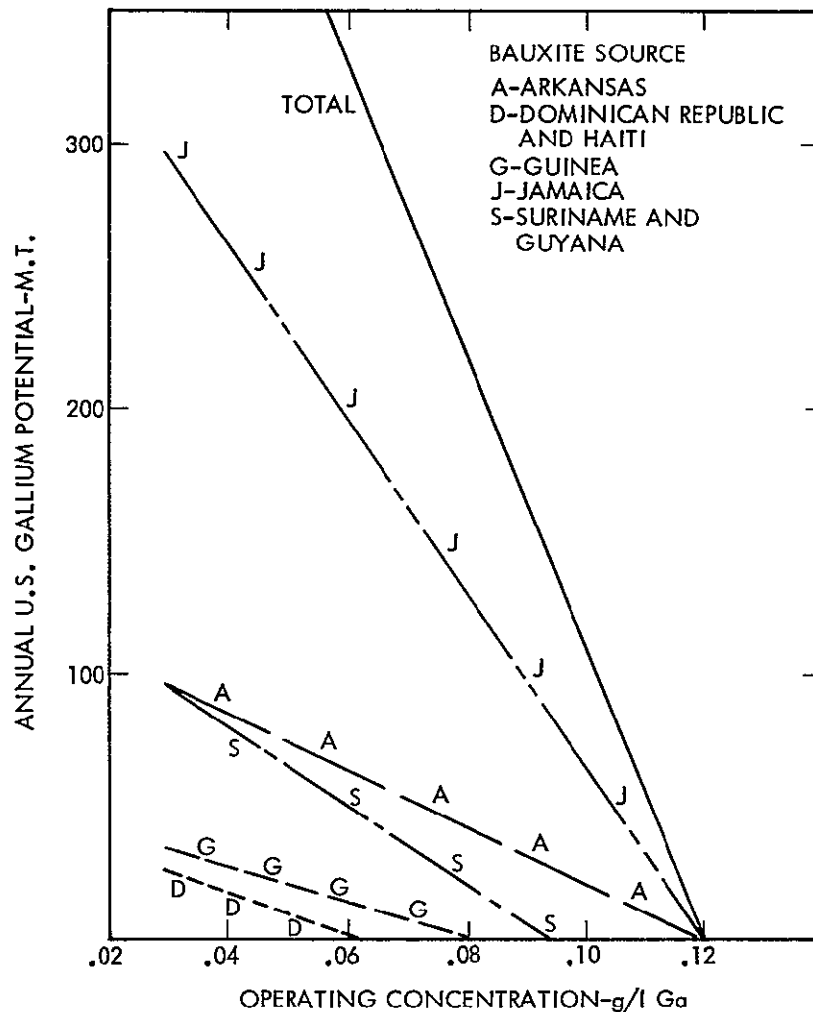


Figure 4-3. Annual United States Ga Potential From Bauxite

To maintain present day prices, the operation should occur at a concentration about 0.05 g/l. Thus, this study suggests an annual domestic potential production of about 350 MT. An extrapolation of these results to estimate world potential should take into account the Ga content of all ores used, but it can be noted that the U.S. production of Al is one-fourth of the total world production.

Actually, Ga is more abundant than tin, silver, indium, or cadmium in the earth's crust. However, since Ga is never found in the free state, the recovery process for each type of ore is important. Gallium is also a byproduct of zinc production, though in a smaller scale than for Al production. No study on zinc ores comparable to the above mentioned on bauxite has been made, but a substantial yearly amount is said to be available from this source (Ref. 27).

Should coal gasification develop into a viable process, a considerable amount of Ga could be obtained according to a recent study (Ref. 28). Commercial methods for recovering Ga from coal ash are in use in England and in Japan. The study estimates an annual production rate of 500 MT assuming that 35% of the U.S. coal processed is available for Ga extraction at an efficiency of 85%.

The number of years that the production of thin-film GaAs solar cells could be maintained depends on the estimated resources, both domestic and world, and on the degree of alternate uses of Ga. Identified world resources of Ga (Ref. 26) are 120,000 MT for bauxite ores and 10,000 MT for zinc ores. The U.S. resources are 2400 MT and 2000 MT, respectively. Potential resources may be about three times as much for zinc ores and five or six times as much for bauxite ores. Professor Anderson's study (Ref. 28) suggests an additional U.S. resource of almost 2×10^6 MT if 60% of the known coal deposits are treated for gasification.

Assuming an annual U.S. production of 500 MT of Ga from both bauxite and zinc ore processing, about 10,000 MW equivalent peak power could be developed yearly from GaAs flate-plate arrays for up to 40 years if no other uses for Ga existed. The use of low concentration such as for hybrid systems would increase the potential annual electrical peak output further even with the increased operating temperatures, and hence, lowered cell efficiencies (Ref. 29, 30). Development of Ga recovery from coal gasification could further double the above annual production rate as well as provide for an indefinite period of production.

Since the GaAs solar cells would have a finite lifetime-hopefully at least 20 years-a large portion of the Ga in these cells and that recovered from the manufacturing process could be recycled. There are several companies which commercially recover Ga from scrap GaAs, including Eagle-Picher Industries, Inc. Presently, about one-third of the waste from the light-emitting diode (LED) market is processed at a cost of about two-thirds the price of new Ga.

Consideration of known competing applications of Ga indicates that the total amount of Ga required annually is relatively small compared to the potential production of 500 to 1000 metric tons. The major uses for Ga are in GaAsP LED displays for watches and calculators, in gadolinium gallium garnet substrates for bubble memories, and in GaAs microwave devices. The peak market for LED displays is only a few years away at which time we might expect to see a saturated replacement and new-buy market at about 20-25% of the peak market. Estimates of peak annual Ga demand for displays range between 20 to 25 MT. The surge of interest in liquid crystal displays in the U.S. may well lower this further.

The potential market for bubble memories and microwave or other GaAs devices is even less certain. If bubble memories were to capture 5% of the total storage market by 1980, the substrate growth would require up to 30 MT per year. However, there are indications that an alternate substrate not requiring Ga may be developed if volume increases enough. No estimates of the Ga requirement for semiconductor devices during the rest of this century exist to our knowledge.

In summary, the total requirements of Ga for applications other than thin-film solar cells are less than one-tenth of the total potential domestic annual Ga production. Substantial resources exist to maintain a production rate of the equivalent of 10,000 MW per year for a period well in excess of the time when recycling GaAs could become a major addition to the supply of new Ga.

C. ECONOMICS

An analysis of the potential cost of a solar cell must consider basically two areas: the cost of materials and the processing costs. Clearly, only the former can be quantitatively discussed, even by estimation at this time of development, for any solar cell. In addition to the cell cost, one must also consider the cost of encapsulation and support structures to arrive at the expected module or array cost. Although neither of the latter two components will be discussed at this time, it should be noted that the eventual encapsulation scheme will quite likely be similar to that (or those) eventually adapted for the Low Cost Silicon Solar Array Project. One exception should be the need for an insulating low-cost module substrate with minimal mechanical support requirements, since the thin-film cell substrate will likely provide adequate rigidity and will be less susceptible to breakage.

Table 4-1 shows the unit costs for the four major materials used in the GaAs thin-film solar cell approach proposed above, the costs per unit area using the assumptions given in the table, and the costs per peak watt for both 10 and 15% efficient devices. These costs are present-day small-lot costs which could conceivably be reduced by a factor of two or more—at least for the chemical elements—if a very large market were developed or should somewhat lower purities be useable. If organo-metallic CVD is desirable, as seems likely, trimethylgallium or triethylgallium will be required in place of the pure Ga metal. The price of these chemicals today is far too high at \$6 to \$10 per gram, but their market is miniscule. With an expanded market entirely new means to form these chemicals, perhaps upstream from the pure refined Ga, may be developed.

The unit costs translate to costs per peak watt of about \$0.14 and \$0.09 for 10 and 15% efficiency, respectively, if a steel substrate proves viable. Figure 4-2 shows that about 0.6% differential expansion will exist between the Ge and steel substrate at the GaAs growth temperature of 650-700°C and nearly 0.8% at the melting point of Ge (942°C). The resultant stresses upon the semiconductors when cooled should be somewhat less serious with an interlayer of Ge acting as a buffer, if a good bond exists between the Ge and substrate. However,

Table 4-1. Unit Costs for the Four Major Materials Used in the GaAs Thin Film Solar Cell Approach

Material	Unit Cost ^a	Cost/Unit Area ^b	Cost Per Peak Watt ^c	
			10% Efficiency	15% Efficiency
Ga (High Purity)	\$0.60/gm	\$3.55/m ²	\$0.036	\$0.024
As (High Purity Arsine)	\$0.22/gm	\$1.25/m ²	\$0.013	\$0.008
Ge (High Purity)	\$0.25/gm	\$6.75/m ²	\$0.068	\$0.045
Si Steel (12 mil) ^c	\$2.40/m ²	<u>\$2.40/m²</u>	<u>\$0.024</u>	<u>\$0.016</u>
Total		\$13.95/m ²	\$0.140	\$0.093
Alternate Substrates ^c :				
Ni/Fe (4 mil)	\$7.20/m ²	\$7.20/m ²	\$0.072	\$0.049
Graphite (125 mil)	\$9/m ²	\$9/m ²	\$0.090	\$0.060

^aPresent day small-lot prices.

^bAssumes Ge and GaAs layer thickness of 5 and 2 micrometers, respectively, and 80% utilization of the chemical elements.

^cNot including passivation treatment or coating.

should this amount of mismatch be intolerable, or if passivation schemes to prevent interaction of Ge with the steel cannot be developed, alternate substrates such as Ni/Fe, Kovar, or graphite may be desirable. The additional substrate costs would then range from about 3 to 4¢ per peak watt, depending on the cell efficiency.

In addition to the above major material costs there will be costs associated with treating the substrate to improve the bonding of the Ge and/or prevent alloying with the substrate*, metallization, anti-reflection coating materials, and of course, the deposition of the semiconductors.

Assuming that a CVD process is required for large scale production, as seems likely, the carrier gas (H_2) must be recycled by cold trapping and palladium purification rather than burned off. The metallization presently used for the Schottky barrier and grid contacts is gold because of its inertness to the air when uncoated. However, much lower-cost metals are being investigated and results will be published in other reports.

The other important factor for obtaining the required low costs is the adaptability of all required process steps to automated continuous or quasi-continuous flow. The process steps envisioned for the thin-film AMOS solar cell (Figure 4-4) are: (1) cleaning or hydrogen firing of substrate material and coating, if required, (2) evaporation or deposition by CVD of Ge, (3) recrystallization of Ge with scanning laser beams, or more likely, with scanning electron beams, (4) chemical vapor deposition of GaAs using organo-metallic sources, (5) oxidation of the GaAs, (6) metal evaporation for Schottky barrier and grid, (7) AR coating evaporation, and (8) cutting (if continuous flow), contacting and interconnecting, and finally encapsulation. With the possible exception of (4), all steps are amenable to continuous-flow processing. Steps (2) to (4) are the only steps involving high temperatures (700-950°C). Since they are sequential steps, a saving in energy for the processing is feasible.

The CVD process has a good potential for scaling up the throughput on a quasi-continuous basis by enlarging the reaction chambers, which would be designed for maximum utilization of the source materials, and by having two or three chambers in each machine working sequentially. No estimates of capital costs for equipment and general operating costs are made at this time. As a general rule of thumb, one might expect that the amortized costs of a fully automated system will be between one and two times the material costs.

In summary, a preliminary consideration of the material availability, materials, costs, and processes required to fabricate thin-film GaAs AMOS solar cells in quantities which would be equivalent to gigawatts of peak power per year is feasible at costs (not prices) between \$0.30 and \$0.40 per peak watt.

*Simple diffusion into the Ge interlayer (Fe, i.e.) should not be a problem because of the relatively low temperatures and the fact that the Ge is not an active part of the photovoltaic device.

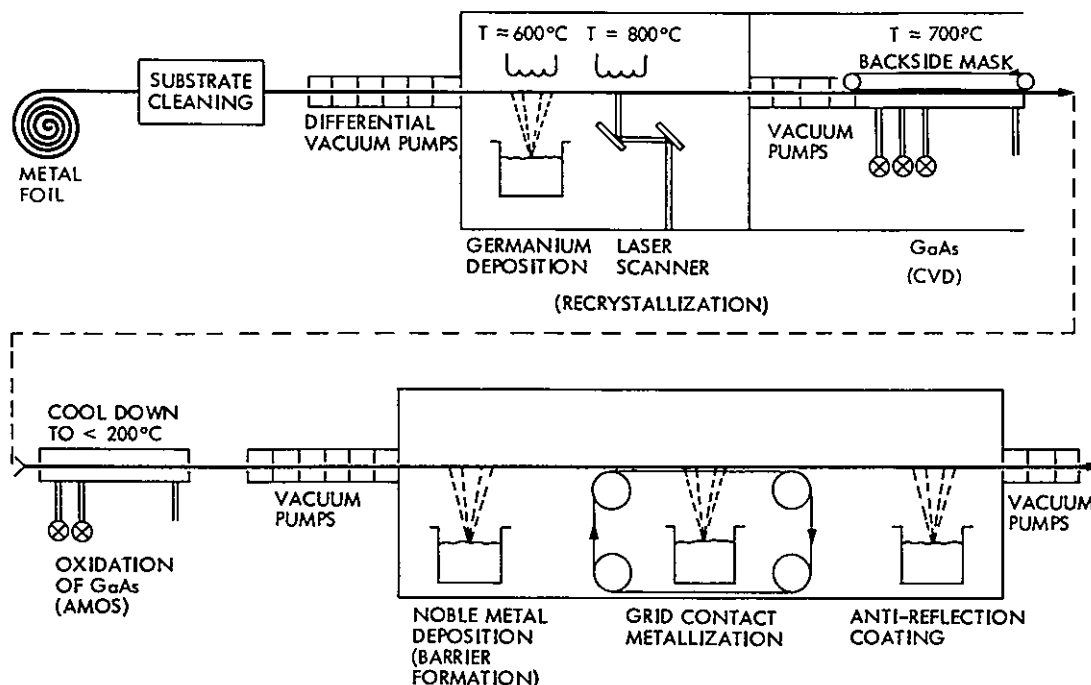


Figure 4-4. Conceptual Thin Film AMOS Solar Cell Production Line

D. GERMANIUM RECRYSTALLIZATION

The properties of the top layer of polycrystalline semiconductor film reflect the condition or quality of the underlying layers and, in particular, the quality of the substrate material. Because of the economic restraints of the terrestrial photovoltaic program, semiconductor films need to be deposited directly on a substrate which is noncrystalline. The use of such substrates leads to very small crystallites or even amorphous layers.

In addition, interaction between the substrate material and the semiconductor at the temperatures of deposition often causes problems due to diffusion of impurities into the semiconductor. Compared to the semiconductor, most low-cost substrate materials have higher coefficients of thermal expansion over the range of temperatures involved (Figure 4-2) leading to cracked, blistered, or peeled layers when cooled to room temperature.

As discussed earlier, a key element in this program is the use of an intermediate layer of Ge in order to alleviate some of these problems and to allow for GaAs films of substantially larger grain sizes with higher quality substructure and electrical characteristics. The cost of the cell will probably be 15-25% higher with the Ge layer, but the development of the thin-film cell should be considerably faster in time

and the ultimate efficiency much higher than without its use. Elimination of the Ge layer as GaAs growth-and recrystallization techniques on low-cost substrates are developed would still remain a possibility.

Although tungsten sheet is prohibitively expensive for solar-cell application, the initial experiments on this program utilized this material for a substrate in order to explore the best means of recrystallizing Ge. Recrystallization of Ge evaporated directly on steel, Kovar, or other Ni/Fe sheet caused unacceptable alloying of the Ge with Fe to date. Means to passivate these metals or the use of graphite substrates will be investigated in following work.

A series of evaporation runs of Ge films were made to determine the preferred orientation, if any, as a function of deposition temperature. To our knowledge the only detailed study of the textural properties of Ge films was performed using quartz as a substrate (Ref. 32). The Ge source was 0.01 ohm-cm n-type polycrystalline material which had been etched in CP4A. The Ge was evaporated in a cold-trapped diffusion-pumped system at 5×10^{-5} Torr using an e-beam gun at 6kV potential. Evaporation rates were 1.4-1.8 m/min with the substrate-source distance at 15 cm. Film thicknesses were of the order of 10 μm .

The tungsten substrates were degreased, cleaned in CP4A followed by hot 10% H_2O_2 and another quick CP4A etch to remove the oxide. Finally, a hot methanol soak, after a deionized water rinse, was made and the surface dried prior to insertion into the vacuum system.

The texture of the Ge films was then investigated with a X-ray line intensity diffraction technique using copper K α radiation having 90% absorption at a depth of about 28 μm . Scans of the (111), (220), (311), (400) and (331) reflection were made and compared with a random 325 mesh Ge powder sample. The latter is used as a standard in order to determine the intensity of each reflection for randomly-oriented crystallites. The intensities of the reflections were determined by multiplying the peak height by the width at half maximum height.

The crystallites were observed to have preferential orientation along the (111) or (110) planes. The films tended to have more (111) orientation as the substrate temperature increased. The (111) preference was also found in the study of quartz substrates (Ref. 32).

Figure 4-5 is a SEM photograph of a fractured edge of a Ge film as evaporated on tungsten. The columnar structure leading to the highly preferred (111) orientation is easily seen. We found that the Ge bonded well to the tungsten if substrate temperatures during evaporation were at least 400°C.

Hall measurements on bridge-shaped samples of as-evaporated Ge films have been made with inconclusive results. Both n- and p-type samples with carrier concentrations between 10^{16} and 10^{18} cm^{-3} were measured (evaporant source was Sb-doped Ge with resistivity of 0.01 ohm-cm). Polycrystalline films often are p-type even if doped with

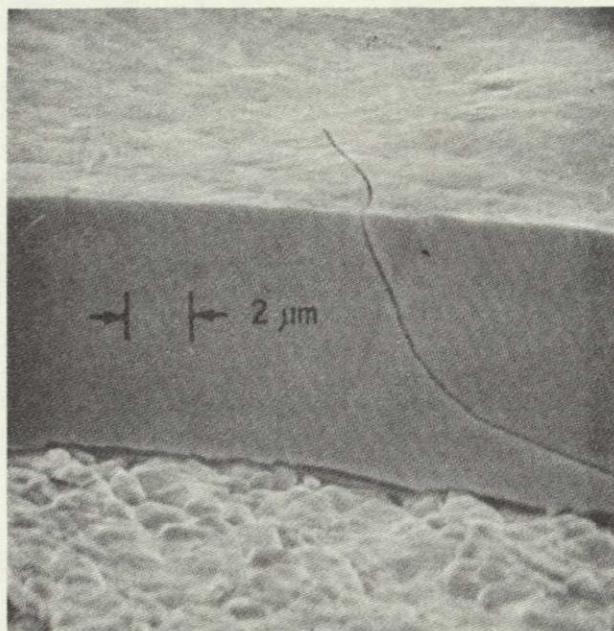


Figure 4-5. SEM Photograph of Fractured GE Film Showing Columnar-Type Growth

donor impurities because of grain boundary effects. Recrystallization will cause the film to maintain the original dopant polarity.

A recrystallization chamber was assembled, first to accommodate a 1000-watt Q-I lamp source focused to a line with about 250 watts per linear inch.* Background heating was supplied through a lower quartz window with a 1000-watt strip heater.** The substrates (2 x 2 cm) were positioned on a graphite susceptor which was translated with a motor-driven translational stage operating a vacuum-type bellows unit at preselected speeds. Forming gas (85% Ar 15% H₂) was used for background atmosphere to minimize oxidation. Calculations showed that radiative heat losses are much larger than losses due to convection and conduction. However, despite the forming gas, some oxidation still occurs on the Ge film. Consequently, a second chamber was built to allow for vacuum operation, although it has not been used during this reporting period.

*Research, Inc. Model 5193-2

**Research, Inc. Model 5305-2A

The line width of the upper lamp at the halfpower points was measured to be 0.40 inches-about four times the specified 0.1 inch. Initial runs with the line heater melted an area considerably larger than the nominal line width preventing true zone recrystallization. Upon solidifying the Ge did show large areas of crystallization and evidence of some dendritic growth with an irregular surface profile. Figure 4-6 shows one region typical of such melts. Grain sizes are more than sufficient for solar cell application; however, the surface is not as smooth as desired for metal-semiconductor cells.

To achieve narrower zone melting, a Nd/YAG CW laser* was leased for evaluation, and later purchased. An optical system was assembled for focusing the laser beam into a thin elongated line by the use of a negative spherical lens and two cylindrical lenses. The recrystallization apparatus was then located under a 45° front-surface mirror which replaced the line heater. Figure 4-7 shows the completed apparatus with laser head and optics. Initially, the laser was operated in TEM₀₀ mode at a maximum obtainable power of 7 watts (CW). The half-power

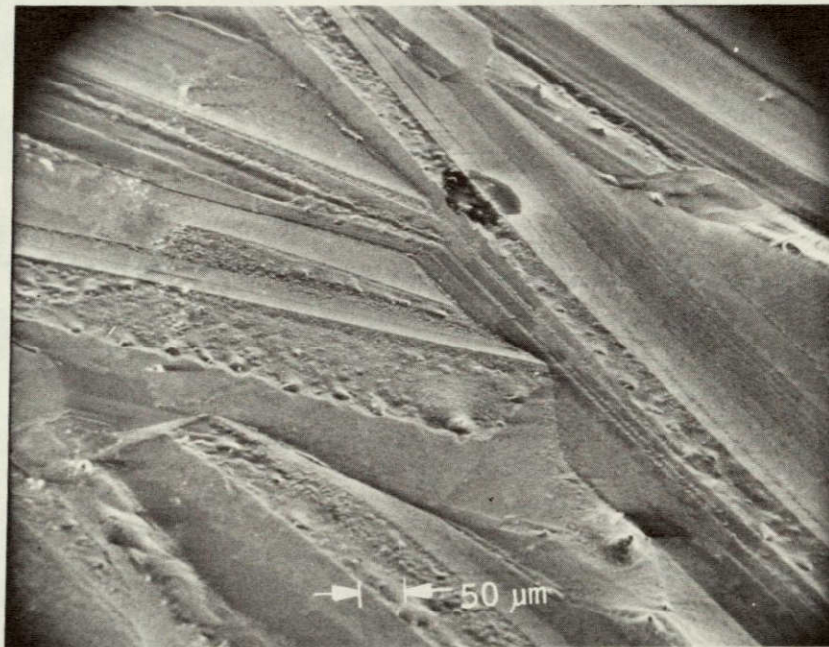


Figure 4-6. SEM Photograph of a Region of Ge Film on Tungsten Melted With a Focused Line Heater. Tilt Angle is 50°

*Quantronix Model 114-2

point width was about 20 μm . Because of the Gaussian distribution in the laser beam, the energy distribution along the length of the line is not constant-being about 50% higher at the center than at the edges. Corrective optics could be designed to smooth out the energy in that direction.

Initial runs (with background heating by a 1000-watt strip heater) would not melt the Ge film unless the line length was reduced to the laser beam spot size of ~ 1 mm. Although the maximum TEM_{00} output we could obtain was only about two-thirds the factory specification of 10 watts, it was obvious that considerably more power was needed, at least for thermally conducting substrates, if a 1-2 cm-wide strip was to be melted. Consequently, the laser was operated in multimode with special larger-radius mirrors installed in order to maximize the multimode output power for a given lamp current. Whereas with the original mirrors about 20 watts was obtained, up to 40 watts could be obtained

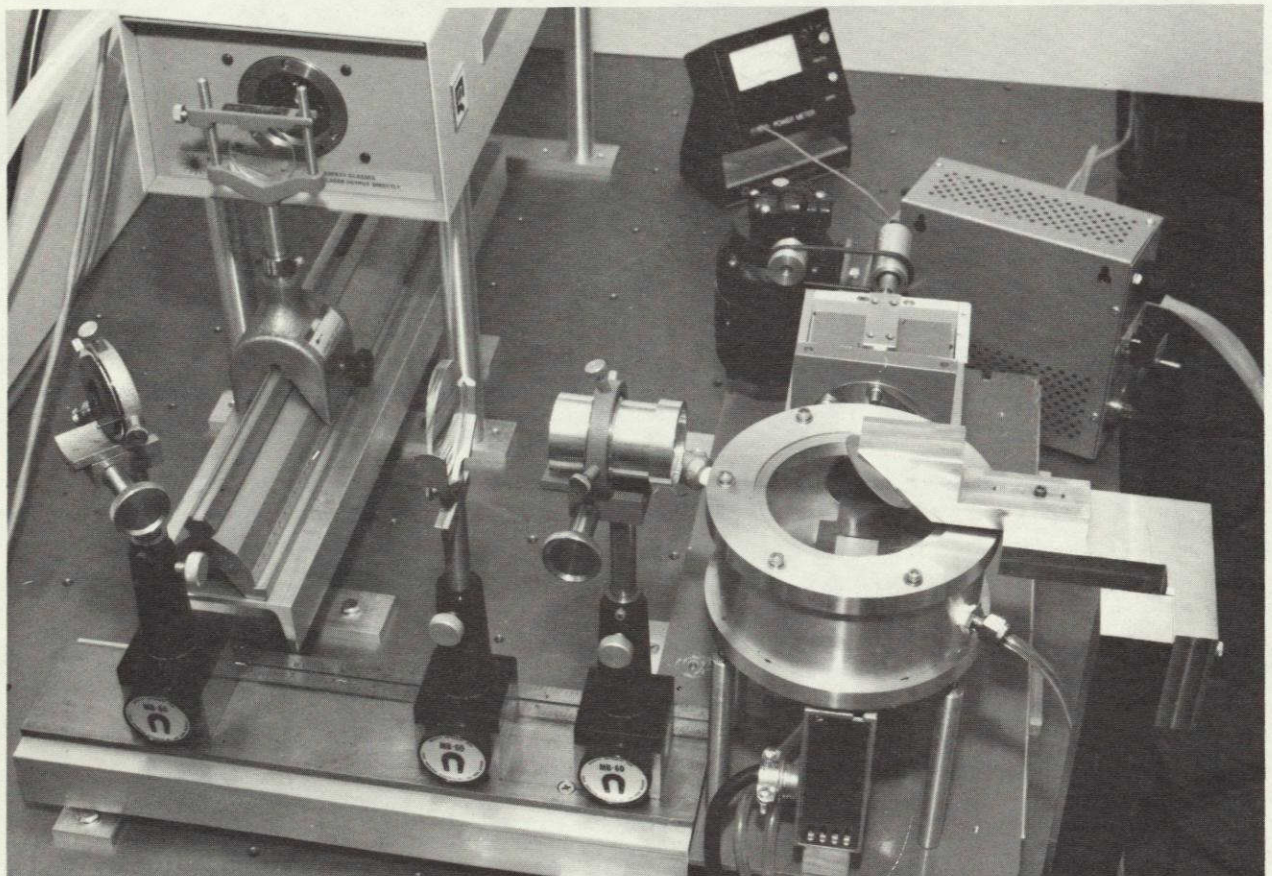


Figure 4-7. Photograph of Laser Recrystallization Apparatus

with the new mirrors. Should it be necessary, a thicker diameter glass rod can also be substituted in the same laser head which can provide up to 100 watts CW in multimode. The half-power point width of 7 mils and the distribution of energy along the length of the focused line is shown in Figure 4-8 (a, b) for the multi-mode output.

Laser recrystallization of the Ge on tungsten substrates showed excellent surface quality and grain growth. However, as will be discussed in the next section, the depth of the molten zone was apparently less than the Ge thickness in places due to the lower power density away from the laser line center. During this phase of laser recrystallization on tungsten, the laser line was about 5 mm in length. The entire 2 x 2 cm substrate was scanned by overlapping the laser lines, translating the substrate 1 to 2 cm per minute, and using a 1000-watt lamp for background heating.

As expected, it was found that the substrate thermal conductivity greatly affects the quantitative amounts of the above variables. For instance, no background heating at all is required for quartz or graphite substrates. There were edge effects in highly conducting

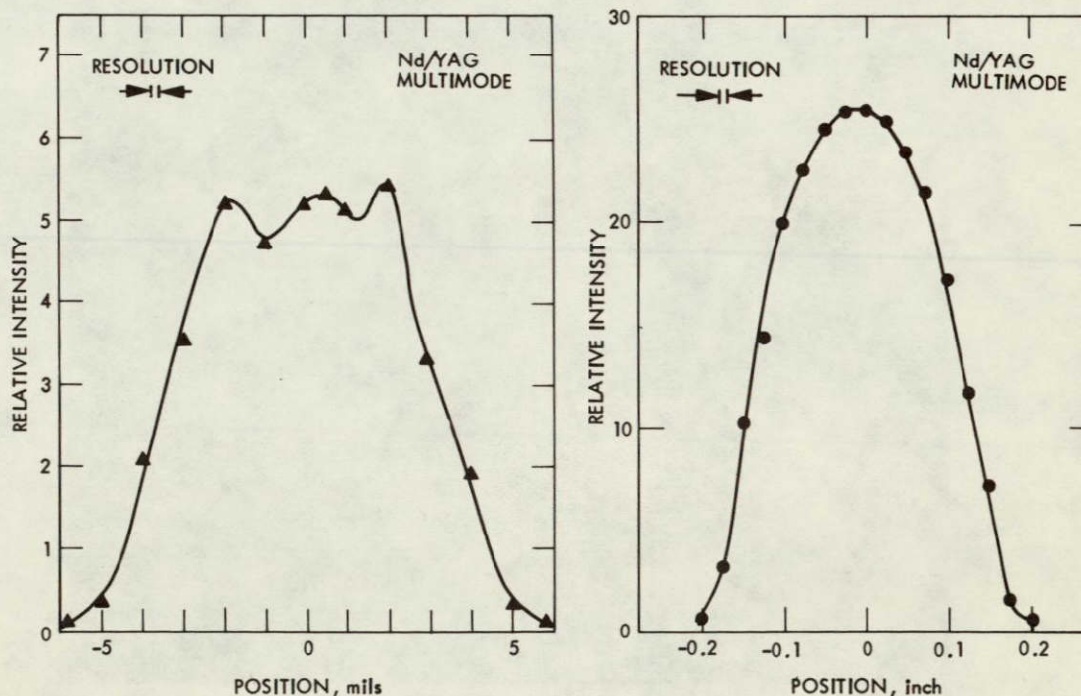


Figure 4-8 (a&b). Beam Profile of Line-Focused Nd/YAG CW Laser Operating in Multimode at About 40 Watts

substrates only in that the higher temperatures at the edge as the laser beam approaches the edge caused a different morphology on the surface within the approximate 1 mm-wide region next to the edge. Such effects would only be present along two edges when continuous ribbon is used in large-scale production, and on those edges, the effect can easily be controlled by intensity profiling of the laser or electron beam.

A photomicrograph of a region of recrystallized Ge on W is shown in Figure 4-9. Typical grain sizes are seen to be some hundreds of microns. The surfaces of the films are sufficiently smooth for fabrication of SB solar cells, although a 5 to 50-second dip etch of $\text{H}_2\text{O}:\text{HF}(10:1)$ was used to bring out detail of the grain structure in the figure. Figure 4-10 shows a profilometer trace of a Ge surface and of the tungsten substrate purposely roughened with an etch. The maximum deflection on the GaAs is seen to be a few micrometers.

The preferred orientation of these Ge films was found to vary unlike the evaporated Ge films before recrystallization. Means to maximize and fix the degree of preferred orientation by variations in the processing or by seeding will be pursued in future work.

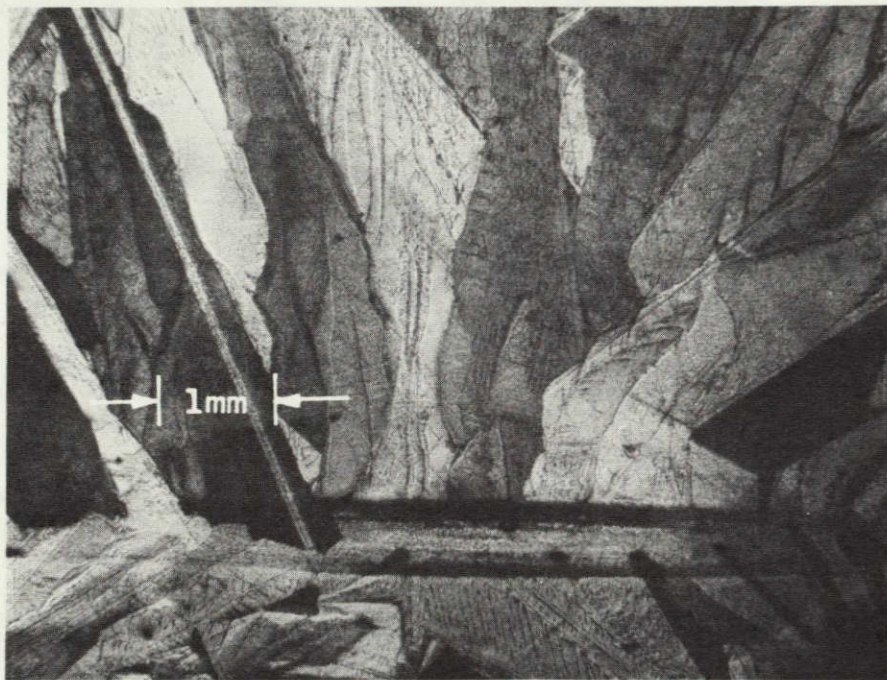


Figure 4-9. Photomicrograph of Laser Recrystallized Ge on Tungsten Substrate

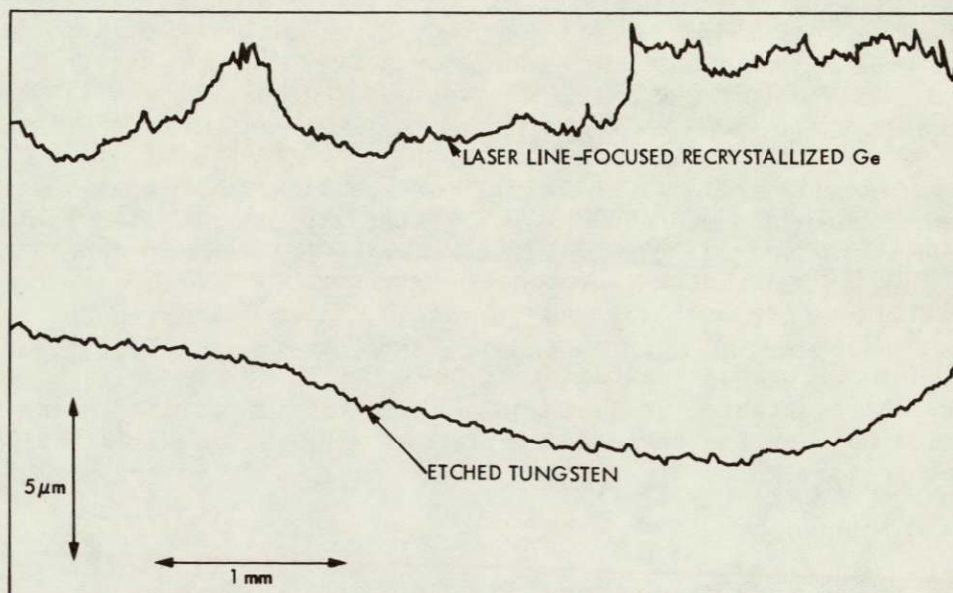


Figure 4-10. Profilometer Trace of Recrystallized Ge on Tungsten Substrate Using Line-Focused Laser Beam and of Etched Tungsten Substrate Before Ge Deposition

In order to determine the doping type and concentration after recrystallization, Hall measurements are required (Schottky barrier heights are too low on highly doped Ge to use capacitance-voltage techniques). Unfortunately, Hall measurements cannot be made on films deposited on conducting substrates. Thus, Ge films in the shape of Hall bars were deposited on quartz substrates and laser recrystallized. The results were not very consistent because of poor bonding of Ge to quartz and some blistering because of the relatively large expansion coefficient difference between Ge and quartz. However, the doping was clearly n-type and carrier concentrations appeared to be greater than 10^{17}cm^{-3} -- similar to that of the Ge source used for evaporation.

Recrystallization of Ge evaporated on untreated Kovar or other iron-based substrates was found to be not feasible. Although the maximum temperature at the Ge-metal interface was under 1000°C , and only for a few minutes, an alloying reaction was always observed as evidenced by a discoloration of the Ge in some areas. The Kovar material used was 25-mil "Kovar A", photo etch quality, with a nominal composition

of 54% iron, 29% nickel, and 17% cobalt. The sheet had been cold rolled and annealed in dry hydrogen at the manufacturer.

No chemical cleaning or surface preparation was attempted in these preliminary experiments since the Kovar was pre-cleaned and protected against handling. However, just prior to the Ge deposition, the substrates were vacuum heat-treated at 700-750°C for two or three minutes. The Ge deposition rate was about 1 $\mu\text{m}/\text{min.}$, as it was for tungsten sheet, while the substrate temperature was held at 400-420°C.

Because Kovar has a thermal conductivity lower than that of tungsten, no background heating with the strip heater was required. Figure 4-11 is a SEM photograph of a recrystallized surface showing alloying of the Ge with components of the Kovar sheet. The darker regions were shown by EDAX (Figure 4-12) to be unalloyed Ge. As mentioned above, means to passivate the lower-cost metals will be investigated in future work.

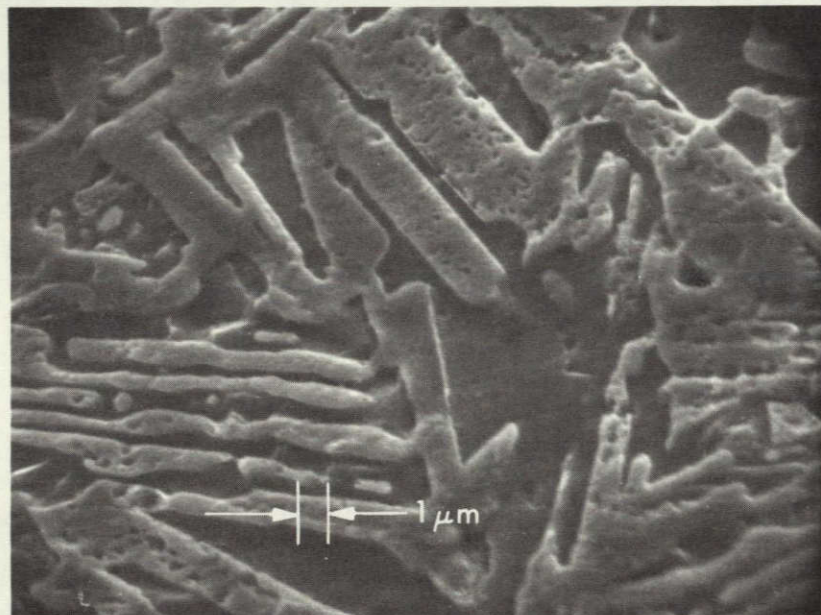


Figure 4-11. SEM Photograph of Ge Alloyed With Kovar Substrate After Laser Recrystallization

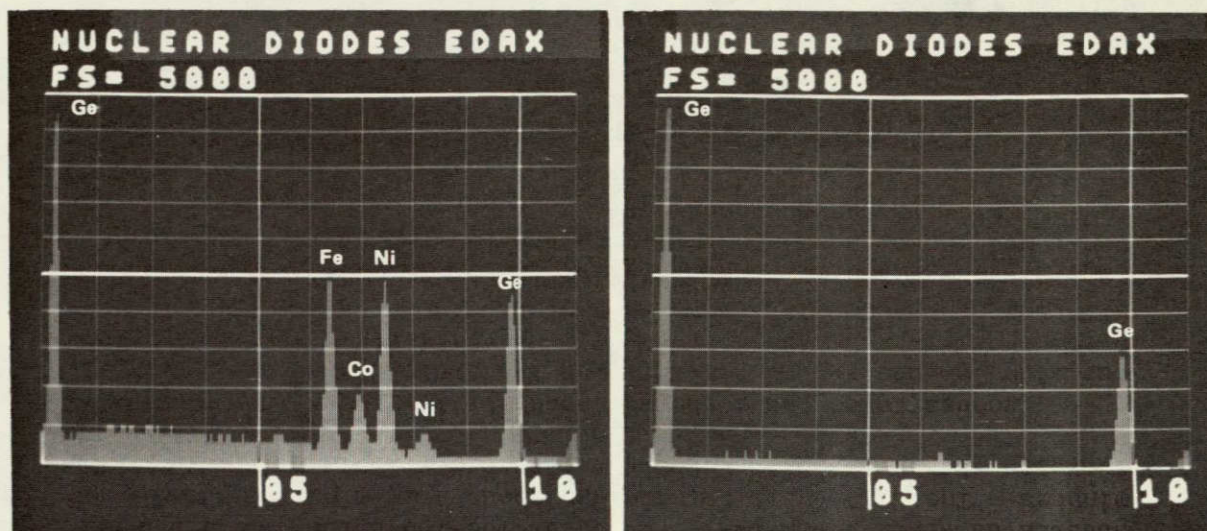


Figure 4-12. EDAX Results on Sample Shown in Figure 4-11:
 (a) Light Regions Showing Alloying, and
 (b) Dark Regions With Unreacted Ge

E. GaAs GROWTH ON GERMANIUM

A capability for growing GaAs by chemical vapor deposition (CVD) did not exist at JPL during this report period. Consequently, a sub-contract (Contract No. 954585) with Electronics Research Division of Rockwell International, in Anaheim, California was initiated in July, 1976 to run through the second half of the one-year NSF grant. For reasons discussed earlier, the preferred CVD technique, assuming that the source material (trimethylgallium) cost can be significantly lowered, is deposition from organo-metallic sources. (Ref. 3).

Most of the GaAs growth was done on single crystal GaAs (100), (111A), (111B), and (110) and on single crystal Ge (100), (111), and (110) in order to obtain baseline film characterization. GaAs layers were also grown on wafers sliced from bulk polycrystalline GaAs in order to improve the short-circuit current output of SB solar cells fabricated to investigate grain boundaries in such material (Section III).

The Rockwell layers grown on poly-GaAs indicated very good minority carrier diffusion lengths (L_p) in that the short-circuit current from standard SB solar cells made on such layers was up to 10% more than that measured for cells fabricated on commercially-grown GaAs

(Applied Materials, Inc.). The doping level of the Rockwell GaAs was measured by capacitance-voltage to be $1-2 \times 10^{16} \text{ cm}^{-3}$ for layers grown on poly-GaAs, whereas the commercial GaAs varied between 2×10^{15} and $2-3 \times 10^{16} \text{ cm}^{-3}$. Thus, the larger current output is not due to an increased depletion width, but rather, due to a longer minority carrier diffusion length.

A series of growth runs were then made on sliced (100) wafers of Ge. All GaAs depositions were performed at 700°C , using 1-2 liter/minute H_2 as a carrier gas mixed with 10% arsine metered for a flow rate of about $175 \text{ cm}^3/\text{minute}$ and trimethylgallium at about $25-40 \text{ cm}^3/\text{minute}$. Typical film thicknesses were about $10 \mu\text{m}$. GaAs films deposited on polished (100) Ge were mirror smooth and exhibited only a few percent less short-circuit current density compared to films grown on poly-GaAs. As expected, films grown on Ge surfaces which were only lapped or lapped and etched had much lower current output because of the residual surface damage. These results are shown in Figure 4-13.

Samples of recrystallized Ge on tungsten were not overcoated with GaAs films on the subcontract in time for discussion in this Final Report. However, one such sample was delivered to Southern Methodist University upon which Profs. Ting L. and Shirley Chu kindly deposited a GaAs film. The CVD growth system at SMU uses halide transport where HCl vapor is passed over heated Ga and the vapor reacted with arsine at the heated substrate. This type of growth reactor has two disadvantages: (1) the HCl vapor may attack the low cost metal substrate, thereby introducing metallic impurities in the GaAs film, and (2) similar etching action on the Ge film will aut dope the GaAs film with Ge from the vapor stream in addition to what will normally diffuse through the interface. The effect should be less than when single crystal Ge substrates are used because only one Ge surface is exposed to the HCl gas, and then only during the initial phases of growth. Nevertheless, the carrier concentrations of the GaAs films were found to be greater than 10^{17} cm^{-3} , presumably due to Ge autodoping from front surface etching by HCl . Consequently, Schottky barrier cells fabricated on these polycrystalline GaAs films had very low current and voltage despite the large grains due to the lowered barrier height and reduced depletion width. Selected small area devices showed open-circuit voltages generally in the 300 mV range with the highest observed value equal to 450 mV (the GaAs was unoxidized). Short-circuit current densities were in the microampere/ cm^2 or, at best, several millampere/ cm^2 range.

These results were expected, and indeed, is mainly the reason for choosing the metal-organic growth system. An unexpected observation, however, was that of a non-uniform growth morphology of the GaAs film. Alternating linear areas of GaAs growth were observed, whereby regions showing mirror-like growth on the Ge grains were separated by darker matte-finish areas. (Figure 4-14). The small area SB devices mentioned above were fabricated in the shiny smooth regions. Devices made in the other regions had no photovoltaic response. It was determined that in these latter areas, the GaAs film was composed of very small crystallites.

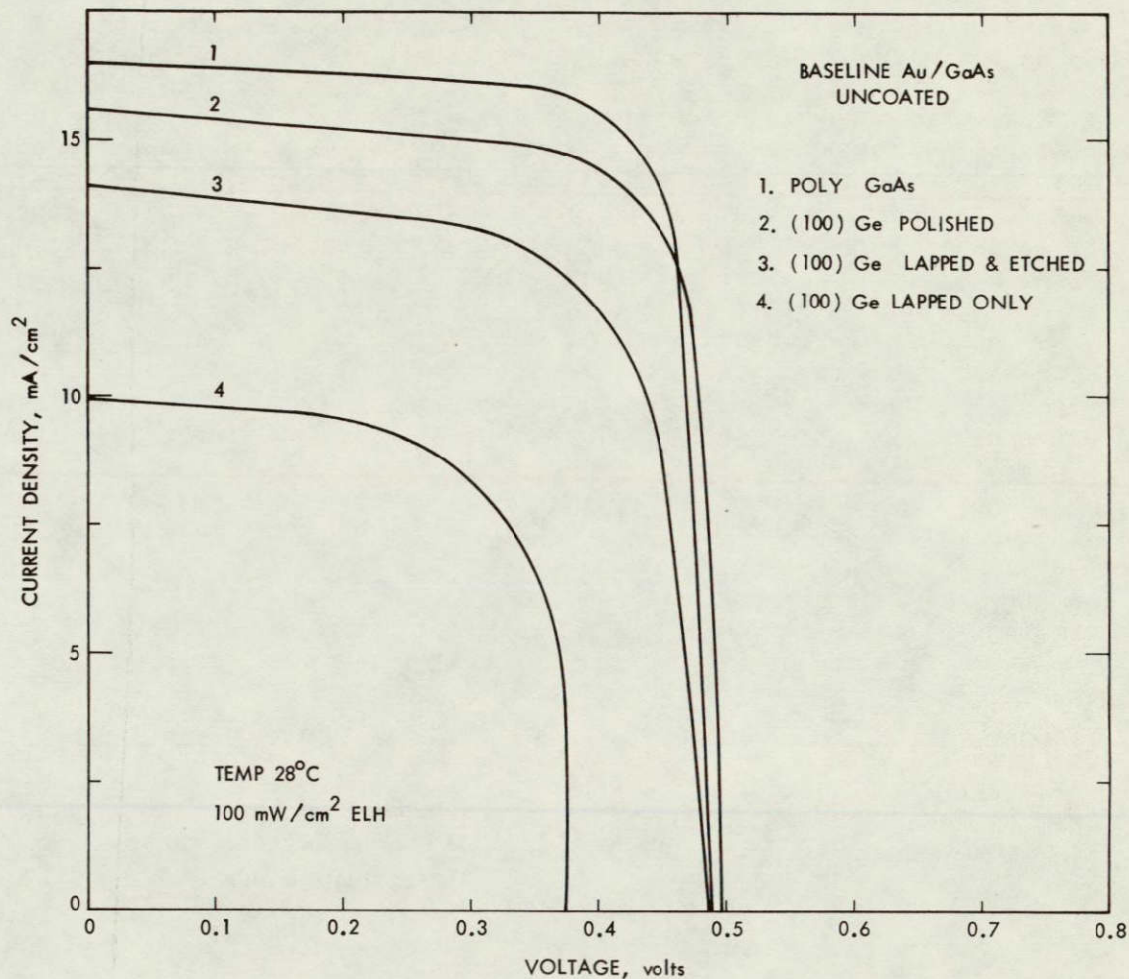


Figure 4-13. Light I-V Characteristics of 60Å Gold on Organo-Metallic Deposited GaAs on Ge Substrates with no Oxidation Treatment Showing Effect of Surface Treatment. Curve 1 is for GaAs Grown on a Sliced Polycrystalline GaAs Wafer

The likely explanation is that the Ge films were not uniformly recrystallized throughout the 10-μm thickness of the film. Regions which only melted near the surface had the as-evaporated Ge surface exposed when the HCl vapor etched the Ge prior to and during the GaAs

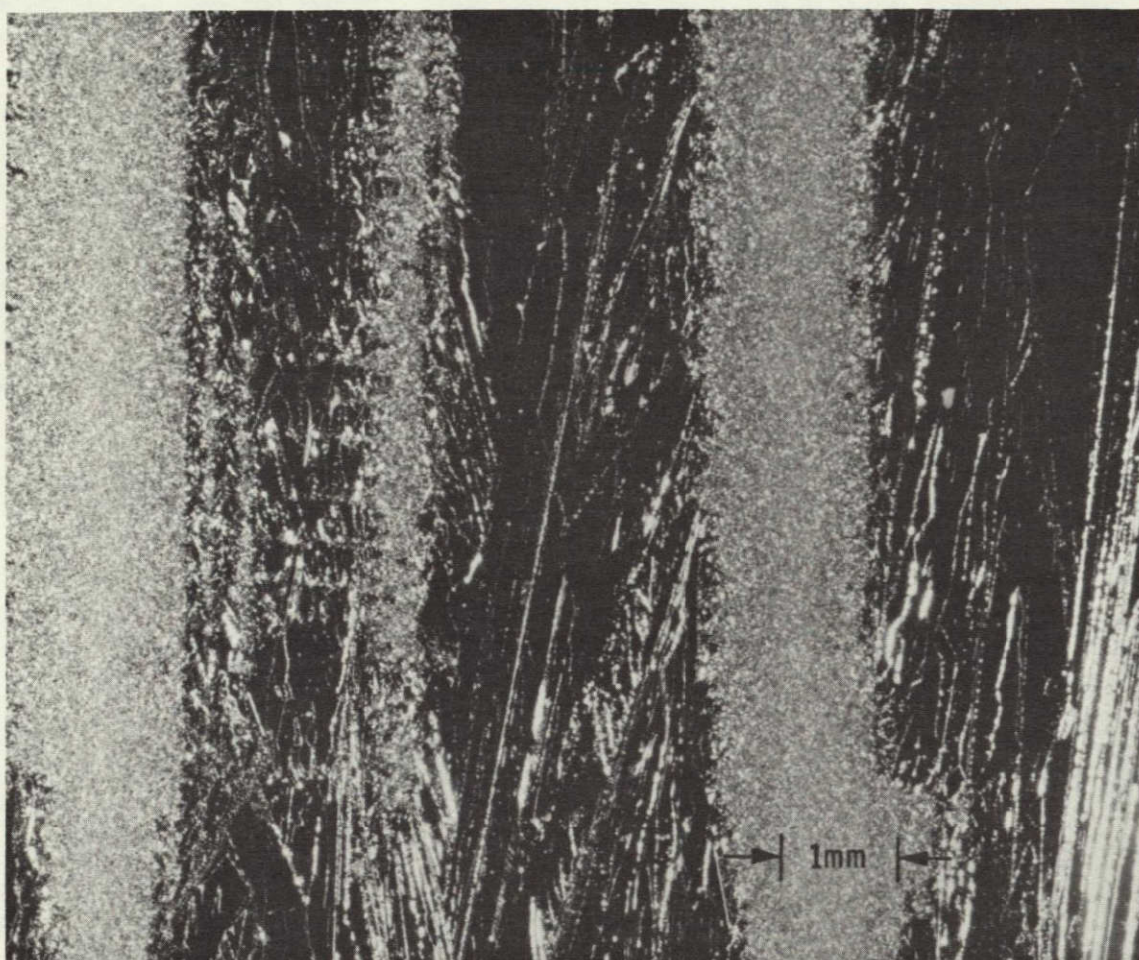


Figure 4-14. Photomicrograph of GaAs Deposited on Laser Line-Focused Recrystallized Ge Films Using the Halide Transport Growth Reactor. The Darker Appearing Regions are Highly Reflecting GaAs Surfaces

deposition.* The reason for the shallow recrystallization is probably due to the highly non-linear energy distribution in the long dimension of the focused laser line (figure 4-8). Despite an overlapping of the individual scan traces, only the central 2 to 3-mm region of each scan apparently had sufficient power density to melt the Ge further from the surface. Even these central areas may not exhibit complete recrystallization throughout the film toward the tungsten surface. Cross-sectioning the films was attempted in order to observe the depth of melting, but difficulty with the tungsten substrate caused "smearing" of the different layers.

*An in-situ 1% HCl in H₂ etch at 740°C for 5-7 seconds is performed prior to initiating the Ga transport.

Complete recrystallization to the metal substrate may not necessarily be required if the as-evaporated Ge film is conducting. However, even with the organo-metallic CVD growth system, chemical etching of the Ge films prior to insertion in the reactor in order to remove the oxide and contamination may also expose regions of fine-grain poly Ge. Consequently, the laser recrystallization system is being modified so that a focused spot can be scanned with a vibrating mirror across one dimension (triangular wave) while the substrate is being translated in the orthogonal direction, as before. This mode should provide uniform power density over the entire sample area with no loss in processing time. The kinetics of zone recrystallization will be greatly changed, however, with the spot velocity being a key parameter. Results will be presented in future reports.

A line-focused scan may still prove to be most desirable for large grain growth, in which case one may: 1) increase the total laser power (for highly conducting substrates) and design corrective optics for uniform intensity, or 2) use line-focused electron beams. The latter will give the most versatility with respect to line thickness control, and hence, degree of temperature gradient along the Ge film surface.

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APPENDIX A

XPS STUDIES OF THE OXIDE-GaAs INTERFACE

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Yeh, Y. M. C., and Stirn, R. J.

I. INTRODUCTION

The oxidation of GaAs has been extensively studied by a variety of methods and, in recent years, has received a great deal of attention (Refs. 1-10). The importance of this research was exemplified by the recent finding that for AMOS (Antireflection-coated Metal Oxide Semiconductor) solar cells, the growth of an interfacial oxide layer increased the efficiency of GaAs Schottky barrier solar cells by up to 60% (Ref. 11). In addition, varying oxide compositions--by utilizing different oxidation techniques and crystal orientations of GaAs--was found to affect the efficiency (Ref. 12).

The purpose of this paper is to demonstrate a correlation between oxide composition and solar-cell efficiency, and to present preliminary results of attempts to chemically alter the oxide composition.

II. EXPERIMENTAL

All oxidized GaAs ESCA samples were prepared at JPL's Photovoltaic Research Lab and were given treatment identical to that received by the solar cells. Samples were then transported to the Surface Analysis Facility in an evacuated desiccator.

Spectra were taken using an HP 5950A ESCA spectrometer. A sample-preparation area was attached to the inlet chamber of the spectrometer, which consisted of a dry box with introduction lock. The dry box was under 5 psi pressure (above atmospheric) of nitrogen, which was dried over LN_2 . Thus, exposure of the sample to atmospheric oxygen, water vapor, and carbon contamination was minimized. Sample temperature was maintained constant during accumulation of spectra by an HP 18621A temperature controller, with thermal stability better than 0.1°K . All samples were run at 250°K , with the exception of reference spectra of As_2O_3 and As_2O_5 , which were accumulated at 200°K . Pressures in the main chamber of the spectrometer were typically $5 - 10 \times 10^{-10}$ torr during accumulation of spectra.

III. XPS RESULTS

XPS studies of the AMOS cell have, thus far, concentrated on oxides grown by water-vapor-saturated oxygen at room temperature on (100), and ozone at 120°C on (100), Ga-rich (111), and As-rich ($\bar{1}\bar{1}\bar{1}$) faces of single-crystal GaAs (with no gold metallization). In both the As 3d and Ga 3d regions of the spectra, a signal assigned to the substrate can be clearly resolved and used as a binding-energy reference. These experiments indicate that the oxide layer has a mixed composition, which includes two arsenic oxides occurring at 3.2 (AsI) and 4.5 (AsII) eV above the substrate As 3d binding energy (40.6 ± 0.1 eV), and two gallium oxides occurring at 1.1 (GaI) and 1.4 (GaII) eV above the substrate Ga 3d binding energy (18.8 ± 0.1 eV).

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Figures A-1 and A-2 show the As 3d and Ga 3d regions, respectively, of GaAs which has been etched (in a dry box) with a solution composed of 0.1% Br (by volume) and methanol, followed by a methanol rinse. Note that there is no detectable oxide. Below each spectrum are the results of deconvolving the instrument function out of the original spectra. The instrument function was determined by taking the derivative of a spectrum of the Fermi edge of Al, and was found to be an asymmetric gaussian with a full width at half-max of 0.56 eV and an asymmetry factor of -0.20. The method of deconvolution will be described elsewhere (Ref. 13). The results show that the As 3d doublet has a separation of 0.65 ± 0.05 eV, in good agreement with the value of 0.69 eV obtained by Bahl, et al. (Ref. 14), while the Ga 3d doublet has a separation of 0.40 ± 0.05 eV--in exact agreement with the value obtained by Lindau, et al (Ref. 15).

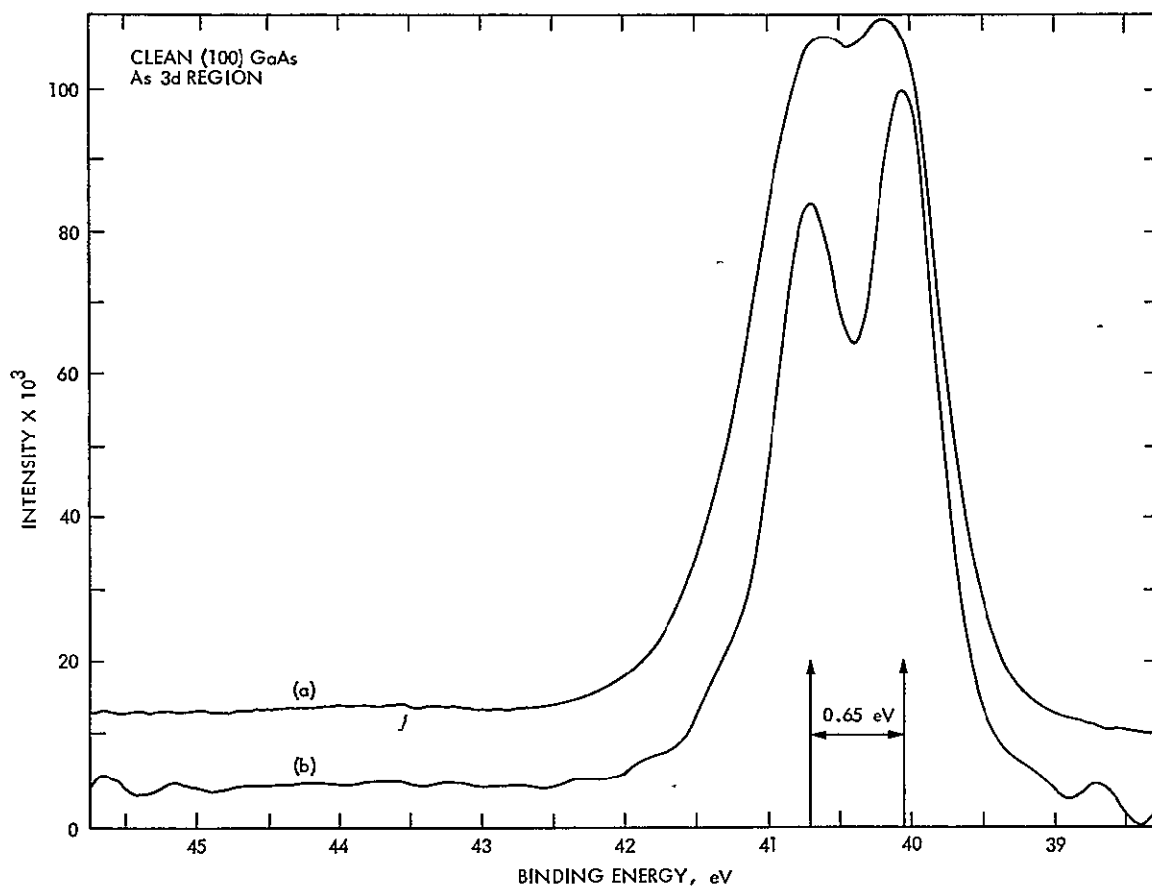


Figure A-1. Narrow scan of As 3d region of clean (100) GaAs
(a) Raw data (b) Deconvolved data

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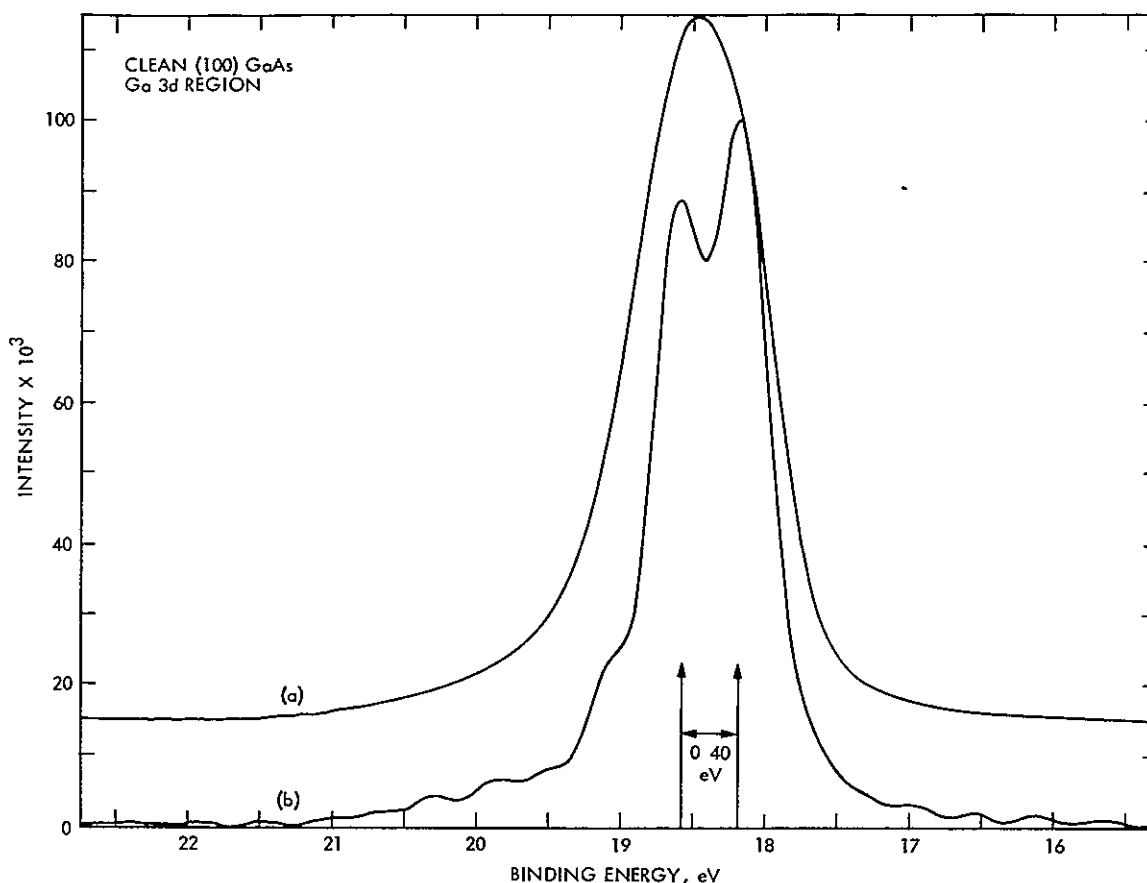


Figure A-2. Narrow scan of Ga 3d region of clean (100) GaAs
a. Raw data
b. Deconvoluted data

Figures A-3 and A-4 show wider scans of the same regions after oxidation, normalized in each case so that the substrate peaks are the same height. From these two figures, it is clear that the two oxidation processes result in radically different oxide compositions, with the ozone process producing both Ga and As oxides in a higher oxidation state (higher binding energy) than the H_2O/O_2 process, and relatively less Ga oxide.

There is a higher than expected intensity in the As 3d region between the oxide and substrate peaks. This is difficult to account for even assuming a high degree of asymmetry in the substrate peaks. This raises the possibility that another arsenic species is present—possibly arsenic metal, as proposed by other researchers (Ref. 5),

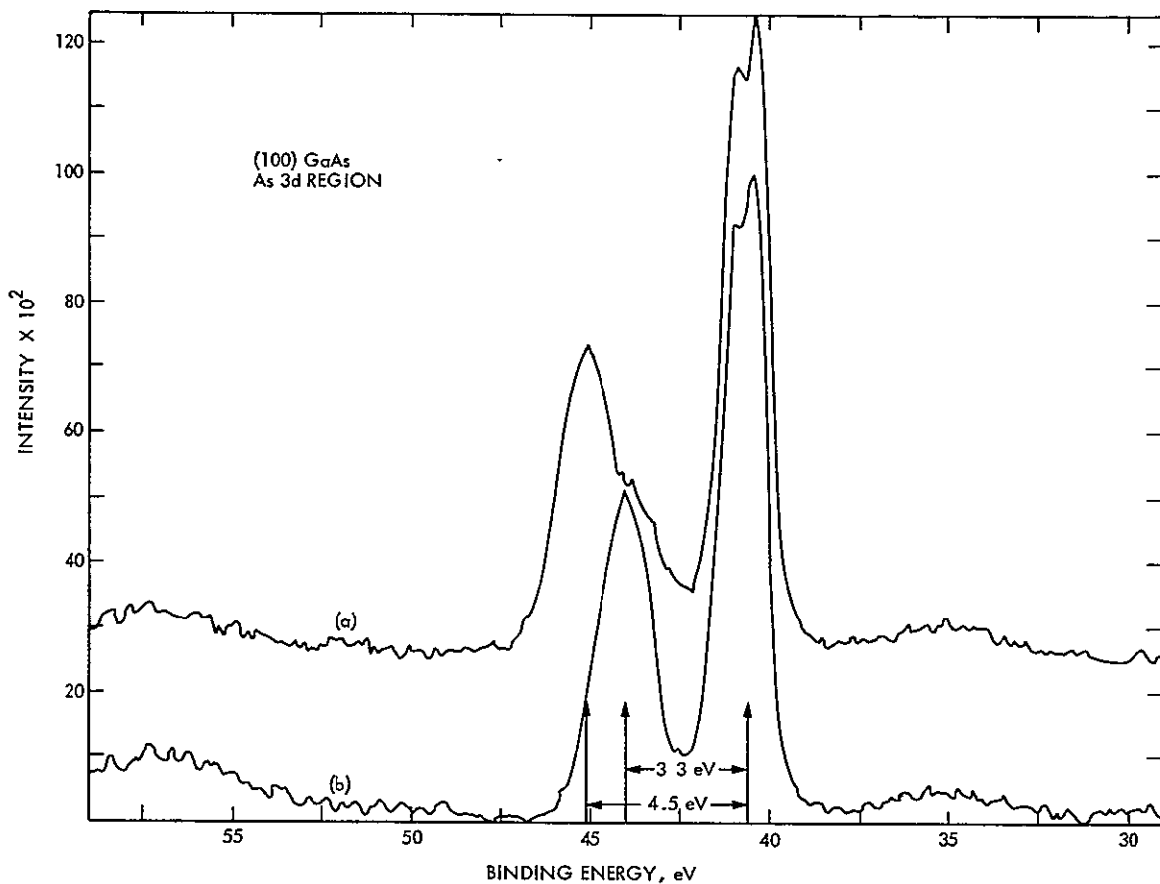


Figure A-3. Wide scan of As 3d region of oxidized (100) GaAs
 a) Oxidized for 20 minutes with ozone at 120°C.
 b) Oxidized for 2 days with water-vapor-saturated oxygen at room temperature.

which would occur 0.6 eV above the substrate binding energy. This would also explain the anomalous intensity ratio $\text{As}3d_{3/2}:\text{As}3d_{5/2}$, which theoretically should be 2 : 3, whereas we observe something closer to 5 : 6. In fact, when a symmetric Gaussian doublet with a peak ratio of 2 : 3 is subtracted from the data, a doublet is observed exactly where arsenic metal would be expected. This argues for small amounts of free As.

In addition to the differing shifts in the $\text{As}3d$ and $\text{Ga}3d$ regions, the two oxidation processes also result in different binding energies in the oxygen's ($1s$) line, which occurs at 531.0 eV for samples treated with $\text{H}_2\text{O}/\text{O}_2$, and at 531.2-531.3 eV for samples receiving the ozone treatment. Reference spectra (taken at 200°K to avoid decomposition)

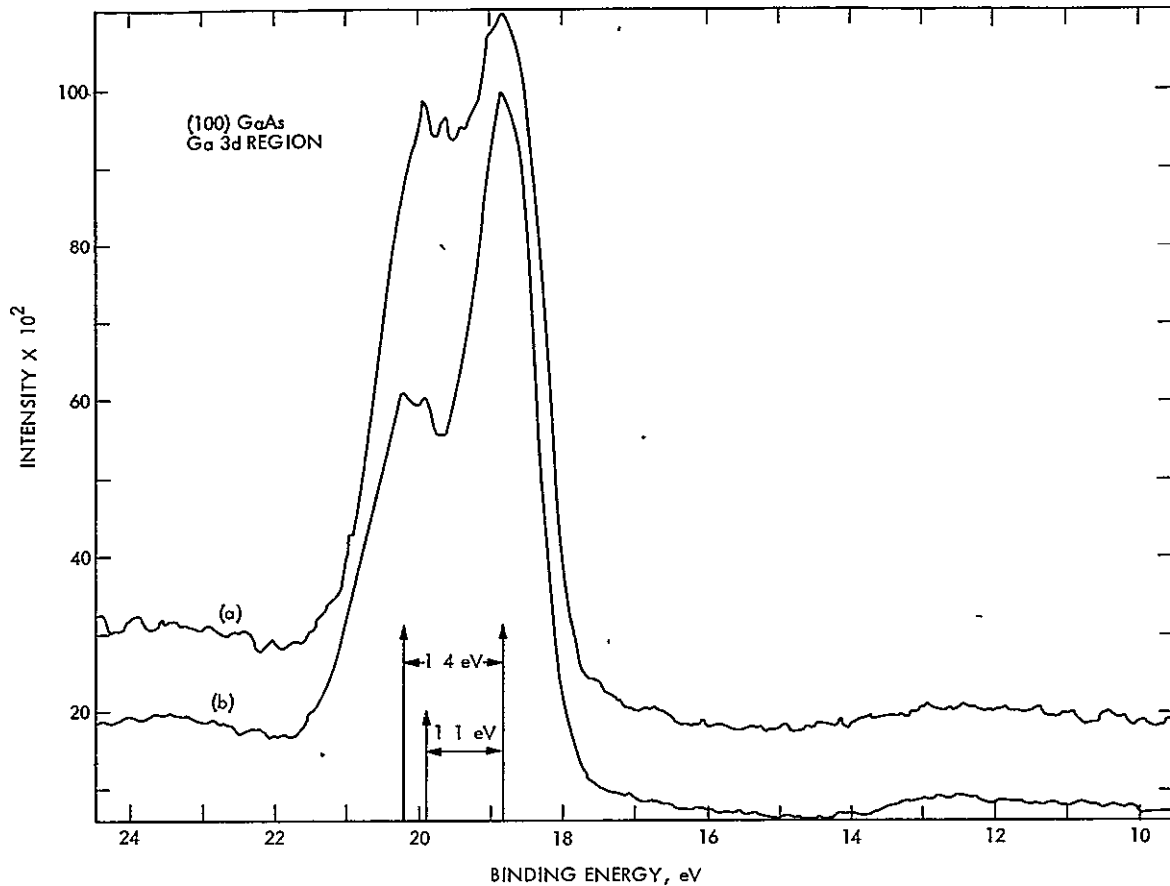


Figure A-4. Wide scan of Ga 3d region of oxidized (100) GaAs
 a) Oxidized for 20 minutes with ozone at 120°C
 b) Oxidized for 2 days with water-vapor-saturated oxygen at room temperature

and values published in the literature show that the most probable oxide composition is AsI = As_2O_3 , AsII = GaAsO_4 , and GaI, GaII are mixtures of Ga_2O_3 and GaAsO_4 (see Table A-1).

Because the two oxidation processes resulted in only slight differences in the O1s and Ga3d regions, the possibility that this was due to sample differences was considered. However, comparing spectra taken from 9 samples treated with ozone (4 (111), 4 $\bar{1}\bar{1}\bar{1}$, and 1 (100)), and 5 samples receiving the $\text{H}_2\text{O}/\text{O}_2$ treatment (all (100)) showed that these slight differences were very reproducible. In addition, 3 samples oxidized with ozone (1 each of (100), (111), and $\bar{1}\bar{1}\bar{1}$) were left in the spectrometer's x-ray beam for several hours, which was found to reduce

the oxide in a manner similar to the reduction of transition metal compounds in the spectrometer observed by other researchers (Refs. 19-23). Concurrent with the reduction of AsII to AsI (see Figure A-5), the 01s and the oxide peak in the Ga3d region each shifted to lower binding energy by about 0.25 eV, implying that the differences are real rather than due to sample differences. That a true reduction is taking place, rather than simple desorption of AsII, is evident by the fact that the AsO_x/As substrate ratio remains constant (as does the GaO_x/Ga ratio), while the O/As substrate ratio decreases--implying something like $2\text{GaAsO}_4 \rightarrow \text{Ga}_2\text{O}_3 + \text{As}_2\text{O}_3 + \text{O}_2$ is occurring.

In addition to differences in oxide composition due to different oxidation techniques, crystal orientation effects were also observed. Comparison of ozone-treated (100), (111), and $(\bar{1}\bar{1}\bar{1})$ faces revealed that the AsII/AsI ratio increases in the order $(\bar{1}\bar{1}\bar{1}) > (100) > (111)$, though this effect is small. More significant is the $\text{AsO}_x/\text{GaO}_x$ ratio, which was found to be about 1.5 for $(\bar{1}\bar{1}\bar{1})$ and (100) and 1.0 for (111), while $\text{H}_2\text{O}/\text{O}_2$ treated (100) had an $\text{AsO}_x/\text{GaO}_x$ ratio of 0.85. From this and the electrical data (Ref. 12), it is apparent that there is a correlation between oxide composition and solar-cell efficiency. Increased efficiency correlates with low AsII/AsI and $\text{AsO}_x/\text{GaO}_x$ ratios.

To verify these trends, an attempt was made to chemically alter the oxide composition. Limited success was achieved. Treatment with a 0.01% (by volume) solution of Br in CCl_4 was found to etch off any remaining oxide and leave in its place a gallium-bromine compound. XPS spectra taken in the Ga3d region reveals a peak occurring at 1.9 eV higher binding energy than the substrate peak (see Figure A-6). In the As3d regions, only the substrate peak is detectable. The GaBr_x was found to dissolve slowly in CCl_4 ; a methanol rinse will remove it completely. Samples treated with Br/ CCl_4 and then oxidized with ozone grow an oxide about 70 Å thick (after a methanol rinse to remove the bromine compound), as measured by ellipsometry, while samples receiving only the ozone treatment do not grow oxides thicker than about 32 Å. The oxide composition is similar to oxides grown by ozone alone, but with much more AsII and GaII. As of this writing, no electrical data is available due to difficulty in obtaining a uniform oxide thickness.

A variation of the above experiments replaces bromine with iodine. Similar results are obtained, with the exceptions that the oxide layer is 40 - 50 Å thick, and no methanol rinse is necessary after oxidation. Spectra taken before oxidation clearly show iodine peaks, but none are detectable after oxidation. The As3d region before oxidation shows only the substrate peak; the Ga3d region has a peak shifted 1.3 eV from the substrate peak which could be a gallium-iodine compound or a residual oxide.

III. SUMMARY

These experiments have indicated that oxides grown on GaAs have a mixed composition; most likely consisting of As_2O_3 , Ga_2O_3 , and GaAsO_4 . Increased solar-cell efficiency has been found to correlate with oxides which are comprised primarily of As_2O_3 and Ga_2O_3 , with little GaAsO_4 .

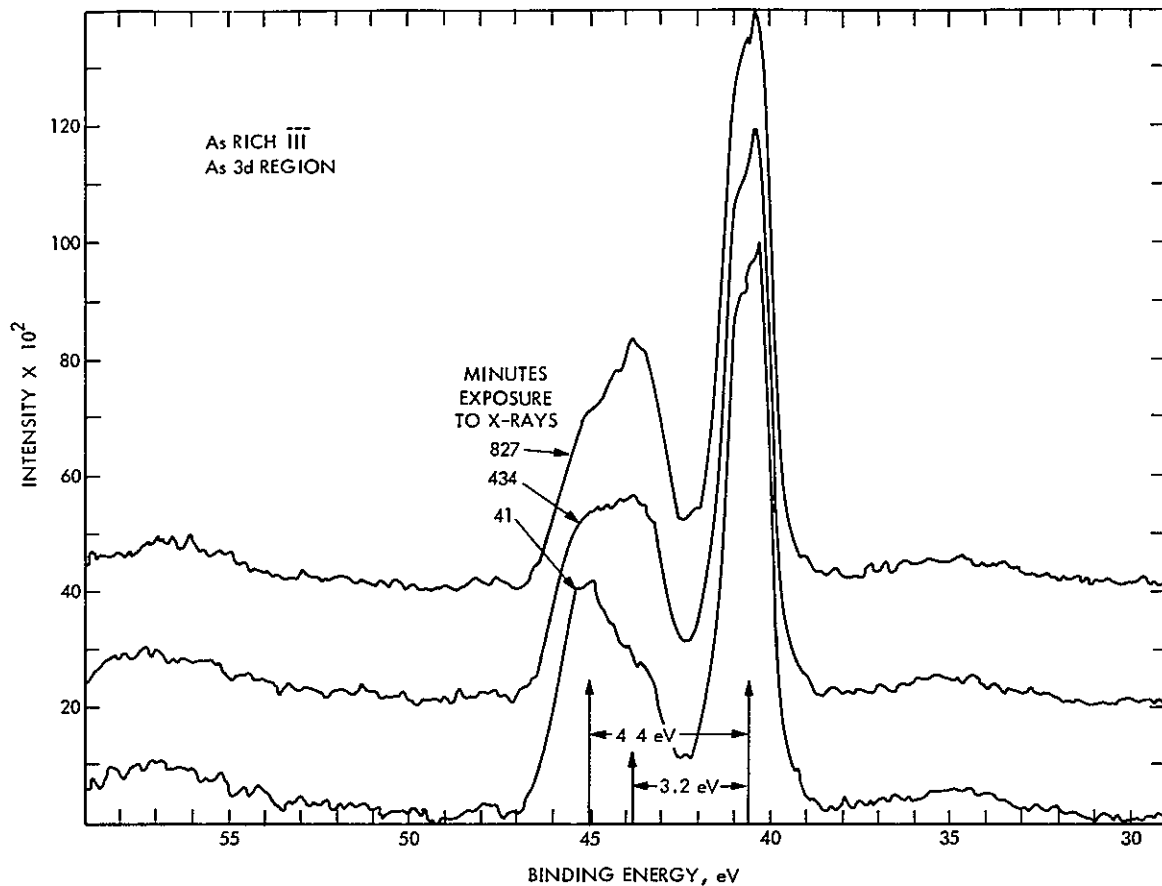


Figure A-5. Wide scans of As region of ozone-treated $(\bar{1}\bar{1}\bar{1})$ GaAs showing reduction of oxide in the spectrometer's x-ray beam

The oxide composition can be controlled to a certain extent by varying oxidation technique, crystal orientation, and chemical treatment. While much work remains to be done in this area, these experiments represent a step towards the ability to grow ultra-thin oxides of nearly arbitrary composition of GaAs.

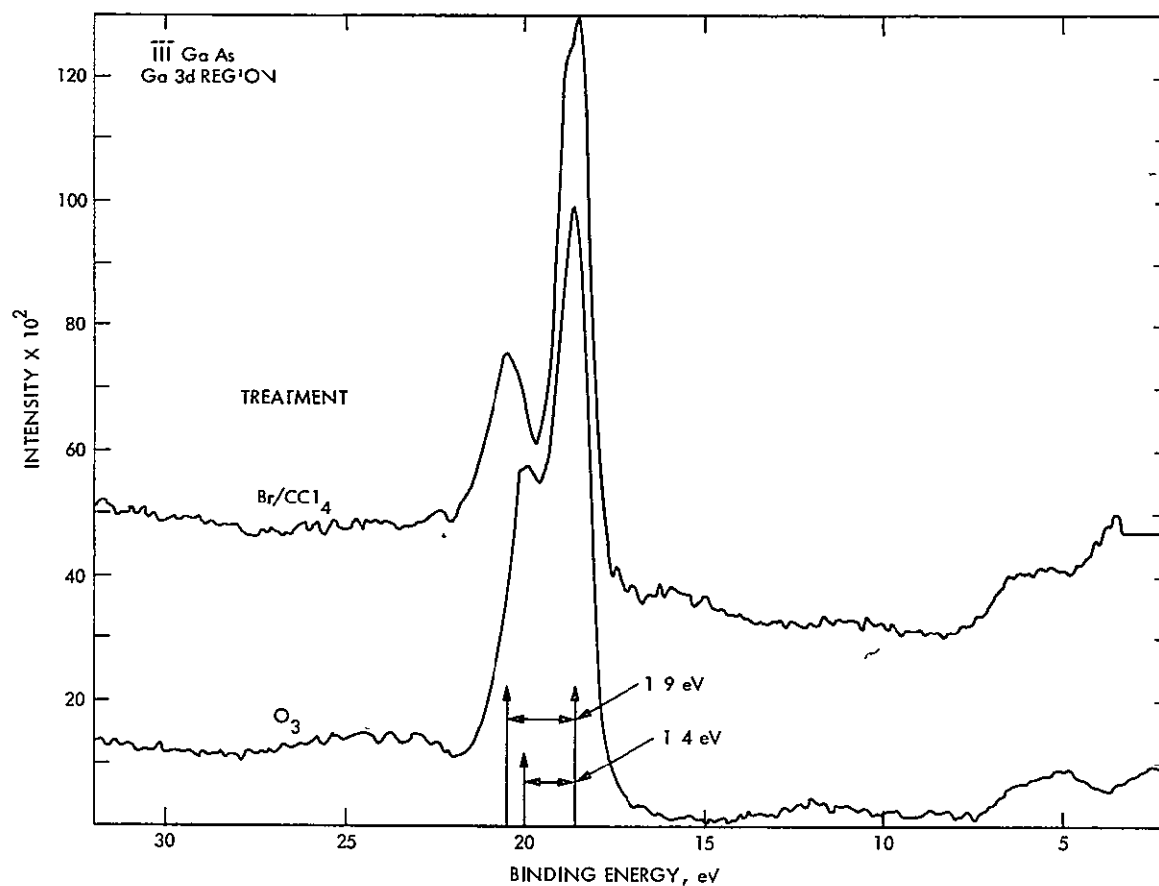


Figure A-6. Wide scans of Ga 3d region of (111) GaAs comparing chemical shifts for ozone-treated and 0.01% Br/CCl₄ treated samples. Peak shifted 1.9 eV from substrate peak assigned as GaBr_x since it appears only in conjunction with a Br 3d peak, and since no shifted peaks are detectable in the As 3d region of samples receiving Br/CCl₄ treatment.

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Table A-1. Observed Chemical Shifts From GaAs Substrate Peaks
(in eV)

	As ₂ O ₃ As 3d	As ₂ O ₅ As 3d	Ga ₂ O ₃ Ga 3d	GaAsO ₄ As 3d	Ga 3d
This work	3.2	5.0	---	---	---
Bahl, et. al.(9)*	3.2	4.9	---	---	---
Leonhardt, et.al.(11)	3.2	---	0.9	---	---
Schon(12)*	---	---	0.8	---	---
Castle & Epler(13)*	---	3.4	1.5	---	---
Pianetta, et.al.(2d)	---	---	---	4.6**	0.9**

*Corrected to take into account a -0.6 eV shift in the As 3d of GaAs from elemental As, and a +1.1 eV shift in the Ga 3d level of GaAs from the Ga 3d of Ga.

**Sample decomposed in spectrometer.

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APPENDIX B
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APPENDIX C

LIST OF PUBLICATIONS

- (1) "The AMOS Cell - An Improved Metal-Semiconductor Solar Cell. Proc. 11th IEEE Photovoltaic Specialists Conference, Scottsdale, Ariz., May 1975, P. 437.
- (2) "A 15% Efficient Antireflection-Coated Metal-Oxide-Semiconductor Solar Cell," Appl. Phys. Letters, 27, 95 (1975).
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