MASTER

HIGH EFFICIENCY THIN-FILM GaAs SOLAR CELLS

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by
Richard J. Stirn

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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FOREWORD

This report describes progress for the first six months of a new task under ERDA/NASA Interagency Agreement EG-77-A-29-1074 for the Division of Solar Energy, now in the Department of Energy. The report was prepared under NASA Contract No. NAS 7-100.

ABSTRACT

A continuation of a solar cell research task previously funded by NSF/RANN was initiated March 1, 1977 for the Division of Solar Energy in ERDA - now Department of Energy. The overall objective is to demonstrate the feasibility of producing high-efficiency (15% or greater) thin-film GaAs solar cells with costs suitable for terrestrial solar electric power generation. The approach is that of growing GaAs by organio-metallic chemical vapor deposition on recrystallized germanium (Ge) films previously deposited on metal substrates and fabricating AMOS (Antireflecting Metal-Oxide-Semiconductor) solar cells on the GaAs.

Previously it had been determined that a water vapor-grown native oxide (temperature = 25°C) was the most useful native oxide for AMOS cells giving open-circuit voltages (V_{oc}) over 800 mV. A new chemical surface preparation prior to oxide growth led to more uniform oxides and reduced interface contamination, yielding lower reverse saturation current densities, a near-unity diode ideality factor, and better reproducibility.

A new method for introducing the oxide interfacial layer - evaporation of Sb_2O_3 from a heated boat - was found to give results equivalent to the native oxide discussed above. Reproducibility is slightly lower probably due to stoichiometry differences in the evaporated film. This development, along alternative metallization, promises a potential for somewhat higher efficiency and increased stability.

Substituting silver (Ag) for gold metallization showed no change in starting cell efficiency, but did greatly improve high temperature stability of the AMOS solar cell. Copper and nickel were found to give lower initial efficiency and aluminum very much lower efficiency. Lifetime testing with these materials has begun as has a study of alternative deposited oxides.

A new study was completed on antireflection coatings on AMOS GaAs solar cells, taking into account the spectral response of the cell and nature of the solar spectra, and the results submitted for publication. It was found that differences in solar spectra ranging from AM0 to AM2 were not significant for practical non-absorbing AR coatings. The ideal coating (index equal to 2.34) reflects

6.8% of the incident useable photons, while a practical coating of index equal to 2.0 only adds an additional 2% loss in short-circuit current J_{sc} (0.5 mA/cm^2). The reflection losses, added to calculated losses due to recombination of minority carriers and absorption in the metal barrier film, gives a calculated collection efficiency of 79.4%—within 2% of the measured value. A low sensitivity of J_{sc} to AR-coating thickness was also found.

XPS (X-ray Photoelectron Spectroscopy) studies had found earlier that the more efficient native oxides had primarily As_2O_3 and Ga_2O_3 with little GaAsO_4 . A new chemical step etching was developed which can be used to profile the oxide in 5- to 7-Å steps without modifying the oxide chemistry as does ion sputtering.

A new Schottky barrier structure is described which can give cell efficiencies up to 16% without oxide interfacial layer effects and 20-22% with a moderate interfacial layer effect. It consists of two semiconductor layers - the bottom layer being GaAs and the upper layer (light incident) $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ with a thickness 1000Å or less. Development will begin when a new CVD growth facility using organo-metallic sources is installed by the end of this first-year program.

AMOS solar cells fabricated on sliced polycrystalline GaAs wafers with 100- to 500-μm grains using Sb_2O_3 deposited oxides showed 14% cell efficiency compared to 16.2% in a region with few grains.

Attempts to laser zone recrystallize Ge films on Kovar or steel failed because of Ge/Fe alloying. Graphite substrates with ground finish did not give large grain growth, whereas vitreous carbon-coated graphite was non-uniform in its wetting capability. Tungsten surfaces still appear to be the best surface for such recrystallization. Studies on means to deposit tungsten coatings economically will be performed in the future.

Four GaAs films grown by organo-metallic CVD on recrystallized Ge with grain sizes many hundreds of microns in length - two each by Rockwell International and two each by Rensselaer Polytechnic Institute - gave similar results when gold Schottky barriers were fabricated on them - shorted or very leaky barriers. The cause of this is unexplained at this time. Only growth conditions normal for growth on single crystal (100) wafers have been used so far.

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SECTION I

INTRODUCTION

A solar-cell research task was begun in January, 1976, under NSF/RANN funding with the following objectives: (1) to investigate the feasibility of growing large-grain polycrystalline gallium arsenide (GaAs) films by chemical vapor deposition on laser beam recrystallized germanium (Ge) layers, (2) to fabricate AMOS (Antireflecting Metal-Oxide-Semiconductor) solar cells on the polycrystalline layers (Fig. 1), and (3) to investigate the physics and chemistry of the oxide-GaAs interface on single-crystal GaAs. Technical overview of the task was transferred to the Division of Solar Energy of the, then existing, Energy Research and Development Administration in August, 1976. A final report has been completed (Ref. 1) describing concepts of the device structure and processing, material availability and cost considerations, results of studies on a variety of oxidation techniques, X-ray photoelectron spectroscopy (XPS) results of the interface chemistry, and effects of melting Ge films on tungsten substrates with line-focused heat lamps and Nd/YAG laser beams.

Figure 1. Thin-film GaAs AMOS Solar Cell.

This report describes progress for the first six months of a new task under ERDA/NASA Interagency Agreement EG-77-A-29-1074 for the Division of Solar Energy, now in the Department of Energy. The task is, in part, a continuation of the previous NSF/RANN task, with an overall objective of demonstrating the feasibility of producing high-efficiency (15% or greater) thin-film GaAs solar cells with costs suitable for terrestrial solar electric power generation. The approach, described in Ref. 1, is that of growing GaAs by organo-metallic chemical vapor desposition (OM-CVD) on recrystallized Ge and fabricating AMOS solar cells on the GaAs (Fig. 1).

Another approach to be investigated somewhat later in the program is the direct recrystallization of GaAs so as to eliminate the Ge interlayer for a savings of up to 10¢ per peak watt.

A third approach embodies a variation of the basic Schottky barrier solar cell in that a second very-thin layer of semiconducting material ($\text{Al}_x\text{Ga}_{1-x}\text{As}$) is inserted between the light-transmitting metal film and the GaAs. The purpose of this "double layer Schottky barrier (DLSB) cell" is to provide a higher open-circuit voltage (V_{oc}) than is normally obtained in a SB solar cell without an interfacial oxide layer. The AMOS structure could additionally be added to the DLSB cell, providing conversion efficiencies well over 20% on single crystals.

This report will also give intermediate results of investigations on GaAs oxidation, antireflection coatings, a new physically-deposited oxide layer AMOS solar cell, device characteristics on bulk polycrystalline GaAs, recrystallization of Ge films, and GaAs growth on such films.

SECTION II
AMOS SOLAR CELL RESEARCH

A. Oxide Interfacial Layer Studies

1. GaAs Native Oxides

A wide variety of oxidation techniques was investigated during the first year of this task (Ref. 1). It was found that oxide growth at room temperature by exposure to water-vapor saturated oxygen ($\text{H}_2\text{O}/\text{O}_2$) was most effective with respect to V_{oc} and reproducibility. During the first six months of the new task, it was found that a new chemical surface preparation prior to intentional oxidation leads to a more uniform native oxide, as well as to reduced interface contamination, yielding lower reverse saturation current, a near-unity diode ideality factor, and a higher degree of consistency after oxidation. The reduction in interface contamination, primarily carbon and nitrogen species, was observed by XPS measurements.

The improved surface preparation, which replaces the previous bromine (1.0%) in methanol etch, is a 15-second etch in NHH ($\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 10:1:1$) followed by a 30 to 60-second etch in SHH ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 10:1:1$). Immediately after etching, the wafers were rinsed in 20-megohm deionized water, and flow-dried with nitrogen gas. Previous work using the bromine/methanol etch gave maximum values of V_{oc} of about 750 mV. With the new surface preparation, values up to 820 mV have been observed (Fig. 2). Presumably, the removal of residual contamination not only yields a more uniform oxide thickness, i.e., reducing the area where more intimate metal-semiconductor contacting is present, but also modifies the interface charge density and its distribution, further enhancing the barrier height. At the same time, interface recombination is greatly reduced. These improvements are responsible for reverse saturation current densities (J_o) as low as the 10^{-14} A/cm² range, equivalent to a barrier height of 1.15 eV. Diode ideality factors for such devices are below 1.1, indicating good Schottky barrier performance with little interface recombination. Large area cell efficiencies up to 17% have been obtained with this processing.

Figure 2. Dependence of V_{oc} and oxide thickness on exposure Time to Water Vapor/ O_2 .

2. Physical Deposition of Oxide Layer

Although the H_2O/O_2 oxidation treatment of GaAs does give reproducibly high cell efficiencies, the oxidation is very time consuming, taking more than 48 hours at 23°C. (Accelerated oxide growth at elevated temperatures degrades the ultimate cell performance.) Consequently, an investigation was started on the utility of evaporated oxide layers. Successful development of such layers could be very significant for several reasons: (1) high speed processing, (2) compatability with other required evaporation steps, (3) potential for further improvements in cell efficiency, and (4) potential for higher temperature and longer life-time operation. The last two points could result from the added flexibility with non-native oxides.

To date, among a limited number of dielectric materials examined for physical deposition, evaporation of Sb_2O_3 from a resistance-heated boat to a measured thickness of 38Å has given the best results. Figure 3 shows the light I-V

characteristic of one of the better 1-cm^2 cells made to date. The highest value of V_{oc} observed has been 830 mV. Fill factor, short-circuit current J_{sc} , diode ideality factor n , and other photovoltaic parameters are comparable, if not superior, to ones obtained with water vapor-grown oxide AMOS solar cells.

Figure 3. Light I-V Characteristics for an AMOS Solar Cell with Sb_2O_3 -deposited oxide.

Figure 4 shows the low reverse saturation current density and n -factor as obtained from the dark I-V characteristic for the same sample used in Fig. 3. Table I summarizes the AMOS results for both oxides and for both surface preparations as discussed above. As stated earlier, it is quite possible that the new etches and extreme care taken for clean handling have reduced contamination at the natural oxide-GaAs interface, leading to the low values of n even after intentional oxidation. Since it is now well established that surface states in GaAs are extrinsic, i.e., only induced by the presence of metals or oxides, unlike the case of silicon, it is also possible that the As_2O_3 -rich oxide, left by the wet-chemistry surface preparations, and the oxide grown by water vapor/oxygen (see Subsection D) induce surface states with appropriate

Table I. Summary of AMOS Results for BM and NHH Plus SHH Chemical Surface Preparation.

OXIDATION PROCESS	CHEMICAL SURFACE TREATMENT	V _{OC} (VOLTS)	FILL FACTOR (%)	DIODE FACTOR, n	REVERSE SATURATION CURRENT (A/cm ²)	EFFICIENCY (%)
WATER-VAPOR OXYGEN	1% BROMINE IN METHANOL	0.67 - 0.76	72 - 81	1.15-1.80	10 ⁻¹⁰ - 10 ⁻¹²	13.4 - 15.7
WATER-VAPOR OXYGEN	NHH + SHH	0.73 - 0.82	80 - 83	1.02-1.10	10 ⁻¹³ - 10 ⁻¹⁴	15.5 - 17.0
Sb ₂ O ₃ DEPOSITION	NHH + SHH	0.74 - 0.83	79 - 82	1.08-1.11	10 ⁻¹² - 10 ⁻¹⁴	15.5 - 17.0

energy level, density and charge state (acceptor-like). These surface states lead to the low J_0 or high barrier height ϕ_B by pinning the metal Fermi level much closer to the GaAs valence band edge than is normally observed. The slow growth of additional oxide by water vapor exposure at room temperature, or by the addition of deposited Sb_2O_3 oxide, filling in areas of non-uniformity in thickness may then serve to assure sufficient metal-GaAs separation, and thus, to prevent introduction of metal-induced surface states further removed in energy from the valence band edge in localized areas.

Figure 4. Dark I-V Characteristics for Sample Used in Fig. 3.

Degradation in V_{oc} and fill factor at elevated temperatures is observed for gold-metallized AMOS solar cells. It is probable that this degradation is due to gold and Ga interdiffusion through the oxide layer. Alternative metals which may minimize this effect will be discussed in the next subsection. The thermal degradation effect with gold metallization appears to be less pronounced for Sb_2O_3 - deposited oxide layers, however. It is possible that the effect can be further minimized by exploring additional dielectric materials for use in AMOS cells, as well as by the use of alternative metals.

B. Metallization

Gold has been used as the barrier metal from the very beginning of the Schottky barrier solar cell research program at JPL. The reasons for this are gold's high barrier height on n-type GaAs and the inertness of gold to atmospheric effect. Additionally, with the discovery of the interfacial oxide layer effect (Ref. 2) giving 60% higher values for V_{oc} , gold was still found to give the best results and to have minimal chemical reaction with the oxide layer.

However, it has long been recognized that gold-GaAs Schottky barriers cannot withstand even moderate temperature without a large decrease in ϕ_B and increase in the diode factor n . Although the exact mechanism for the degradation is uncertain, it is known to be associated with a large interdiffusion of gold into the GaAs bulk and Ga to the surface of the gold contact (Ref. 3). Some studies have shown that a tungsten interlayer between the gold and GaAs will allow operating temperatures up to 500°C (Ref. 4). The barrier height is actually formed by the tungsten metal, however, and such an approach is not desirable for solar cell applications because of light-transmission losses. More recently, it was discovered that saturating the gold film with Ga metal and flash-evaporating the alloy onto GaAs will prevent Ga out-diffusion, even at temperatures as high as 400°C, (Ref. 5). The values of ϕ_B and n were found to be only slightly modified after one hour at 300°C. The concept of Ga-saturated barrier metals is perhaps applicable for a number of metals. However, the fact that the barrier metal film is only 50-100Å and, therefore, is quasi-continuous must be considered.

In any case, it is very desirable to find an alternative metal because of economic considerations. The use of a 100Å-thick gold film on polycrystalline GaAs would require 1280 grams of gold per megawatt of electricity at 15% efficiency. Because of the evaporation process using shadow masking, a considerably larger amount than is needed would be deposited on other surfaces, requiring expensive reclaiming costs. Because of these considerations and the desire to find a metal which can demonstrate long lifetimes at elevated temperatures (in conjunction with an, as yet to be determined, optimum physically deposited interfacial layer), a study was begun to examine alternative metals-particularly very low cost base metals.

Although silver (Ag) is still a relatively expensive metal, it was used for both the thin film and grids in the first attempts to substitute for Au. It was found that the initial photovoltaic parameters were virtually the same as when Au was used. In fact, the cell used for Figs. 3 and 4 to demonstrate the new deposited oxide technique has Ag front contacts. It was found that Ag will withstand 100°C temperatures for considerably longer periods than Au. Nevertheless, degradation in cell characteristics - primarily fill factor and V_{oc} - slowly began after several days' exposure to 100°C temperatures. Further tests are now in progress, using encapsulated cells so as to eliminate water-vapor or oxygen interaction with the interfacial region.

During this reporting period, copper (Cu) and aluminum (Al) were also briefly investigated. Earlier work had shown that Al-GaAs Schottky barriers had better high-temperature durability than did Au or Pt, for example (Ref. 3). However, Al was found to give considerably lower values of ϕ_B and, hence, V_{oc} , on oxidized GaAs-with either the native or deposited Sb_2O_3 oxide layer. This is in contrast to results on cleaved GaAs (Ref. 6), which showed that Al only gave about 0.10 volt lower barrier height than did Au or Pt. It is quite possible that the Al metal chemically reacts with the oxide layer, modifying the interface state charge distribution. Activities to investigate the chemistry of the metal-oxide interface with XPS are planned.

Unlike Au or Ag, Al shows a significant difference between the As_2O_3 - rich water vapor-grown native oxide and the deposited Sb_2O_3 oxide (Figs. 5 and 6). This fact may indicate a chemical reaction effect, as referred to above, rather than simply a low metal work function effect. In the same figures, the light I-V characteristics obtained for Cu barrier metallization are also shown. The V_{oc} values obtained for both Cu and Al are considerably more varied run-to-run than is the case for Au or Ag. The studies with alternative metals, should be considered only preliminary, since their behavior has to be considered in conjunction with the oxide layer chosen.

Figure 5. Some Alternative Metals on Sb_2O_3 -Deposited Oxide AMOS Solar Cells.

Figure 6. Some Alternative Metals on Water-Vapor-Grown Oxide AMOS Solar Cells.

C. Antireflection Coatings

Because a GaAs surface metallized with 60 to 100Å of Au or Ag reflects over 45% of the useful solar energy, an antireflection (AR) coating is a vital component of the AMOS solar cell. An earlier study (Ref. 7) showed how an ellipsometric technique can be used to determine the optimum refractive index and thickness of an AR coat to be applied to a metal-oxide-GaAs structure. Thus, for example, an index of 2.34 is ideal for 60Å-thick gold on GaAs.

These studies have been extended to include the actual spectral response of the solar cell and the nature of the solar spectra. The wavelength appropriate for minimum reflectance was calculated for several solar spectra for AR coatings with the ideal 2.34 refractive index, as well for practical values of the index (about 2.0). Such values are usually obtained by conventional deposition techniques without any high temperature processing. Values of J_{sc} , the short-circuit current, were then calculated for several combinations of the two types of AR coatings and for AMOS solar cells having ideal and practical collection efficiencies. These current densities were then compared with maximum theoretical current densities obtainable with several solar spectra so as to obtain information on the magnitude of losses due to reflectance and to other effects. The results, which have been submitted for publication, are given following a discussion of the approach.

An optimum AR coating of a solar cell maximizes the short-circuit current density J_{sc} . The current density depends not only on the optical characteristics of the AR coating, but also on the spectral distribution of the sunlight and absolute spectral response of the uncoated solar cell. An expression J_{sc} can be written as

$$J_{sc} = \int_0^{\infty} I_{ph}^i(\lambda) \frac{\eta(\lambda)}{1-R_1(\lambda)} [1-A_2(\lambda)-R_2(\lambda)] d\lambda, \quad (1)$$

where $I_{ph}^i(\lambda)$ is the spectral current density ($A/cm^2/nm$), assuming each photon contributes to one electron-hole pair. The index i represents the desired solar spectrum and equals 0,1,2 for Air Mass Zero, One, and Two, respectively. $\eta(\lambda)$ is

the measured spectral response (number of minority carriers collected per incident photon as affected by the minority carrier diffusion length, depletion width and recombination rates at the surface) before AR coating, $R_1(\lambda)$ is the fractional reflectance of the MS solar cell before AR coating, $A_2(\lambda)$ is the absorption loss caused by the addition of the AR coating, and $R_2(\lambda)$ is the reflectance of the MS solar cell after AR coating.

The absolute spectral response is negligible for wavelengths longer than λ_g -the wavelength corresponding to the photon energy equaling that of the semiconductor bandgap. Assuming zero absorption losses introduced by the AR coating for photons with wavelength of interest, eq. (1) can be approximated by

$$J_{sc} = \int_0^{\lambda_g} I_{ph}(\lambda) \eta'(\lambda) [1-R_1(\lambda)] d\lambda, \quad (2)$$

where $\eta'(\lambda) = \eta(\lambda)/[1-R_1(\lambda)]$ is the absolute spectral response assuming no reflection. This quantity warrants special attention, since it represents the upper limit for any solar cell having zero reflectance [$R_2(\lambda) \equiv 0$].

Table II, which is presented in Ref. 7, shows the maximum value of J_{sc} for GaAs and Si and the incremental current densities theoretically obtainable at all wavelengths less than 500 and 400 nm, as well as the total incident power and "usable" power, considering the semiconductor band gap.

The method to obtain single-layer ideal AR coating parameters (refractive index and thickness) for the MS solar cell is summarized in the following:

- a. Determine the spectral response $\eta(\lambda)$ and the fractional reflectance $R_1(\lambda)$ of the solar cell without AR coating.
- b. Measure the equivalent complex index of refraction of the uncoated solar cell by ellipsometry (Ref. 7), calculate $R_1(\lambda)$ and compare with measured values in order to validate the ellipsometric measurement.
- c. Calculate the ideal AR coating refractive index and thickness for zero reflectance at a number of wavelengths by using

Table II. Total and Useful Power, Maximum Values of A/W
Incremental Maximum Current Densities, and for Three Solar Spectra.

P_{Total} (mW/cm ²)	P_{useful} (mW/cm ²)		$\left(\frac{A}{W}\right)_{\text{useful}}^{\text{maximum}}$		I_m (mA/cm ²)		ΔI_m (mA/cm ²) $\lambda < 500$ nm		ΔI_m (mA/cm ²) $\lambda < 400$ nm	
	GaAs	Si	GaAs	Si	GaAs	Si	GaAs	Si	GaAs	Si
AM0 ^a 135.3	83.5	102.0	0.401	0.524	38.5	53.4	10.1 26.2%	18.9%	3.26 8.5%	6.1%
AM1 ^b 92.5	61.3	73.5	0.483	0.537	29.6	39.4	6.11 20.6%	15.5%	1.26 4.3%	3.2%
AM2 ^c 74.9	48.7	58.8	0.496	0.550	24.2	32.3	4.08 16.9%	12.6%	0.62 2.6%	1.9%

$$N_{AR} = \left(n_o \frac{V^2}{(U-n_o)} + U \right)^{1/2}, \quad (3)$$

$$t_{AR} = \frac{\lambda}{2\pi N_{AR}} \tan^{-1} \left(\frac{N_{AR} (U-n_o)}{n_o V} \right), \quad (4)$$

where N_{AR} and t_{AR} are the refractive index and thickness of the ideal AR coating, respectively, n_o is the refractive index of the medium through which the light is transmitted; U and V are the real and imaginary parts of the measured equivalent complex index of refraction $N(\lambda)$ of the uncoated cell, respectively.

- d. Calculate the fractional reflectance $R_2(\lambda)$ as a function of wavelength for each pair of AR coating parameters.
- e. Calculate the short-circuit current J_{sc} from equation (2) for each pair of AR coating parameters, considering both the absolute spectral response and solar spectrum.
- f. Determine values of AR coating parameters that yield maximum J_{sc} by iteration.

In practice, the index of refraction for the ideal AR coating derived from the method described above may lie outside the range of the values for available materials. The material with index of refraction closest to the value for the ideal AR coating, yet with minimum absorption loss within the range of wavelengths of interest, should then be chosen. The required thickness for minimum reflectance at a given wavelength of the AR coating with this practical index of refraction can now be obtained, instead of calculating for zero reflectance as shown in step (c). All other steps can be carried out in the same manner.

For most MS solar cells, the equivalent complex index of refraction is relatively constant over an appreciable range of the solar spectrum (Ref. 7). Hence, as an approximation, one can use the index of refraction obtained at the He-Ne laser wavelength (6328Å), for example, as the index applicable to the whole

range of the solar spectrum. In this approximation, step (b) in the ideal case can be performed at the single wavelength of 6328Å.

Gold was used for this study because of its inertness to the atmosphere during the measurements. An uncoated cell consisted of a 60Å-thick gold film which was vacuum-deposited at a 10Å/s rate on an oxidized n-type GaAs substrate, using a resistance-heated source. The deposition was done in an ion-pumped vacuum system equipped with a Kronos Model ADS-200 digital quartz crystal thickness monitor, which had been previously calibrated, using multiple-beam interferometry.

To obtain the single-layer ideal AR coating parameters for the solar cell, a Hilger and Watts prism monochromator was used to measure the relative spectral response. Subsequently, a Spectra Physics Model 164 ion (krypton or argon) laser was used to properly scale the relative spectral response to provide the absolute spectral response $\eta(\lambda)$ of the solar cell. The fractional reflectance $R_1(\lambda)$ was measured as a function of the wavelength, using various laser wavelengths (Fig. 7). For completeness, the equivalent complex index of refraction ($N(\lambda) = U(\lambda) - jV(\lambda)$) of the uncoated Au-GaAs AMOS cell is also shown in the figure. The index of refraction was obtained by using a Rudolf Model 43603 ellipsometer with a resolution of $\pm 0.01^\circ$ and equipped with a variable-wavelength compensator.

Figure 7. Equivalent Complex Index of Refraction and Reflectance Dependence on Wavelength for an Uncoated AMOS Solar Cell.

The earlier work (Ref. 7) showed that ideally N_{AR} should equal 2.34 in order to achieve $(R_2)_{min} = 0$ for the case of 60Å-thick gold on oxidized GaAs. Index of refraction values higher than 2 can be obtained for vacuum-deposited dielectric films with high-temperature treatment. High-temperature treatments are not desirable for Schottky barrier devices, however. Typical index values are about 2 for practical vacuum-deposited dielectric films (Ta_2O_5 , Sb_2O_3 , Nb_2O_5 , TiO_2) using e-gun, resistive heating or laser flash deposition. Values of the index and thickness of the dielectric films were measured by ellipsometry. The values of thickness were further confirmed by multiple-beam interferometry.

The short-circuit current J_{sc} was calculated, using steps (a)-(f) given above. The results for three different solar spectra are presented in Table III, along with the AR-Coating Center Wavelength (ARCW) (the wavelength at which the reflectance is minimum). The calculations were performed for both the practical AMOS solar cell using the measured spectral response, and an ideal AMOS solar cell having 100% collection efficiency. The maximum short-circuit current density possible for GaAs with no losses (J_m) is given in Table II.

(1) AR Coating Center Wavelength (ARCW)

One interesting result of the calculations is that the difference between the optimum ARCW for different solar spectra is relatively small when no additional absorption losses are present due to the AR coating. In fact, when the ideal or practical AR coating is tailored for AM1 sunlight (ARCW=580 or 588 nm, respectively) and the AMOS solar cell operated under AMO or AM2 sunlight, the value of J_{sc} is reduced by only 0.1% from the corresponding optimum values. Also note in Table III that the change in optimum ARCW due to the use of the practical AR coating ($N_{AR} = 2.0$) is only about 7nm for any one of the solar spectrum. Figure 8 shows the calculated J_{sc} versus ARCW for the practical AR coating case. The broad maxima indicate the low sensitivity of J_{sc} to the exact value of ARCW.

Table III. Short-Circuit Current and ARCW Values for Optimum AR Coatings

	NO REFLECTANCE	IDEAL AR COATING [$R_2(\lambda)_{\min} = 0$]				PRACTICAL AR COATING ($N_{AR} = 2$)	
	PRACTICAL AMOS CELL	IDEAL AMOS CELL [$\eta'(\lambda) = 1$]		PRACTICAL AMOS CELL		PRACTICAL AMOS CELL	
	J_{SC} (mA/cm ²)	J_{SC} (mA/cm ²)	ARCW (nm)	J_{SC} (mA/cm ²)	ARCW (nm)	J_{SC} (mA/cm ²)	ARCW (nm)
AMO	32.6	35.4	555	30.2	562	29.7	570
AM1	25.5	27.6	576	24.0	580	23.5	588
AM2	20.9	22.7	594	19.8	594	19.5	600

Figure 8. Short-Circuit Current Density Dependence on Ar Coating Center Wavelengths of an AMOS Solar Cell with AR coating Having a Refractive Index of 2.0.

(2) Short-Circuit Current Density

Figure 9 shows the measured spectral response $\eta(\lambda)$ of the AMOS solar cell with gold metallization before AR coating as well as the spectral reflectance $R_1(\lambda)$ presented earlier in Fig. 7. When a single-layer AR coating with a refractive index of 2.0 is applied, giving a coated reflectance $R_2(\lambda)$ (Fig. 9), the resulting absolute spectral response $\eta''(\lambda)$ is as shown in Fig. 9. This response can be defined as

$$\eta''(\lambda) = \frac{\eta(\lambda) [1 - R_2(\lambda)]}{[1 - R_1(\lambda)]} \quad (5)$$

The previously defined "ideal" spectral response $\eta'(\lambda)$, which assumes zero reflectance at all wavelengths, is also shown in Fig. 9 for comparison.

Figure 9. The Measured Spectral Response and Reflectance of an Uncoated and AR-Coated AMOS Solar Cell.

When these various spectral responses are multiplied by the spectral current density representing the desired solar spectrum (Ref. 7) and an integration made over the wavelength (eq. 2), one obtains the short-circuit current densities for the uncoated cell and those given in Table III. For example, the uncoated AMOS solar cell under AM1 sunlight is calculated to have a value of J_{sc} of 14.6 mA/cm²—very close to the measured value (Ref. 8). When a practical AR coating with $N_{AR} = 2.0$ is applied, the J_{sc} increases by 61% to 23.5 mA/cm² (25.4 mA/cm² for 100 mW/cm²).*

* Notice that in this example, the ARCW is 60nm, instead of the optimum 588 nm; yet, the value of J_{sc} is nearly identical (23.51 versus 23.53 mA/cm²).

Several observations can now be made. Again using the AM1 example, but for the optimum SRCW, we see that by comparing the absolute maximum current J_m for no losses (Table II) with J_{sc} calculated for an ideal AR coat ($N_{AR} = 2.34$) on an ideal AMOS solar cell [$\eta'(\lambda) \approx 1$ for $0 < \lambda < \lambda_g$] (Table III), the difference is 2.0 mA/cm^2 or 6.8%. This amount is the minimum loss in J_{sc} due to reflection from a single-layer AR coating. For the case of a practical AMOS solar cell (one which has losses due to photon absorption in the gold film and non-ideal collection efficiency of minority carriers) with an ideal AR coating, the total loss in J_{sc} is 5.6 mA/cm^2 or 18.9%, and 6.1 mA/cm^2 or 20.5% with a practical AR coating. Consequently, the fact that AR coatings with less than ideal N_{AR} must be used leads only to an additional 0.5 mA/cm^2 loss in J_{sc} (for AM1).

Comparing the calculated J_{sc} for a practical AMOS solar cell with practical AR coating (Table III) with the calculated J_{sc} for a practical AMOS solar cell with no reflection losses, one determines that the loss in J_{sc} attributes to reflection losses by the practical single layer AR coating is 2.0 mA/cm^2 . Current loss attributable to recombination of minority carriers and photon absorption in the metal* is 4.1 mA/cm^2 , as seen by comparing J_m (Table II) with column 1 in Table III (AM1). The sum of these two loss mechanisms leads to what is called the collection efficiency - defined by the short-circuit current density J_{sc} divided by the total possible current, if every photon-generated electron-hole pair is collected (J_m). The calculated collection efficiency of 79.4% (23.5 mA/cm^2 divided by 29.6 mA/cm^2) for AM1 spectrum agrees within 2% of the measured value. The results given above are very similar for the cases of AM0 and AM2 solar spectra.

The relatively low sensitivity of ARCW to the air mass and J_{sc} to refractive index N_{AR} would cause one to suspect a similar low sensitivity of J_{sc} to the AR coating thickness (t). Indeed, calculations show that a 10% error in t leads to only a 1% reduction in J_{sc} . Even for 20% error in t , the reduction is still less

*Separation of the two losses experimentally is impossible. The potential loss in current due to photon absorption in the metal film is no doubt partially reduced by the collection at the interface of hot electrons generated in the metal film.

than 3%. Therefore, critical AR coating thickness control is not required during GaAs AMOS solar cell processing.

To verify the validity of the approximation of using the index of refraction obtained by the He-Ne laser (6328Å) as the index applicable to the whole range of the solar spectrum, Fig. 10 shows comparative short-circuit currents versus ARCW for both the approximate calculation (curve 1) and complete calculation (curve 2). The calculations show that: 1) optimum ARCW values are essentially identical, 2) the approximate calculation will overestimate the maximum short-circuit current by only 1.3%, and 3) maximum deviation in short-circuit current over the range from 0.4 μm through 0.9 μm for ARCW is less than 3%.

Table 10. Short-Circuit Current Density Calculation vs ARCW comparing Single-Wavelength Determination of Equivalent Cell Refractive Index with Wavelength-Dependent Index.

(3) Summary and Conclusions

Methods for designing an optimum single-layer AR coating for GaAs AMOS solar cells were described, using ellipsometric techniques described earlier (Ref. 7) to determine the cell's effective index of refraction. Considering both the

spectral response of the solar cell and the solar spectrum, the appropriate wavelength for minimum reflectance (ARCW) was calculated for AR coatings with ideal refractive index ($N_{AR} = 2.34$) and with the more commonly obtained index of 2.0. The optimum wavelength values were found to be nearly the same for AM0, AM1 and AM2 solar spectra for both coatings. Therefore, the use of AR coatings designed for AM1, for example, will provide a satisfactory optical match to AM0 or AM2 spectra.

Values of short-circuit current density J_{sc} were calculated for GaAs AMOS solar cells with known spectral response and with practical AR coatings. These results were compared with both practical and ideal (no collection efficiency loss) GaAs AMOS solar cells, using ideal AR coatings or practical AR coatings. It was found that the ideal AR coating will reflect 6.8% of the usable incident photons. Use of the practical coating only adds an additional 2% loss in J_{sc} . The calculated collection efficiency of about 80%, including reflection losses, agrees well with the measured value. Generally, it was shown that J_{sc} is not sensitive to either the ARCW or the AR-coating thickness. In addition, the use of the index of refraction measured at a single wavelength (6328Å) was demonstrated to be adequate in the design of an optimum AR coating for Au-GaAs AMOS solar cells.

D. XPS Studies

Objectives of the XPS (X-ray Photoelectron Spectroscopy) studies are: (1) to apply existing surface analysis techniques and develop profiling techniques as required for the study of the thin interfacial layers of AMOS solar cells, (2) to determine the layer composition as a function of processing, (3) to determine the chemical reaction of these layers with the GaAs surface and with the metal contacts, and (4) to develop "in-situ" techniques for depositing controlled layers as a reference for comparative study.

The reader should refer to Ref. 1 for details of the investigations prior to March, 1977. Briefly, the studies indicated that water vapor/ O_2 oxides grown on GaAs at low temperatures have a mixed composition - consisting of As_2O_3 , Ga_2O_3 , and $GaAsO_4$. Increased solar cell efficiency was found to correlate with oxides which are comprised primarily of As_2O_3 and Ga_2O_3 , with little $GaAsO_4$. The oxide composition can be controlled to a certain extent by varying oxidation technique,

i.e., by water vapor/ O_2 , ozone, glow discharge O_2 , or anodization, by crystal orientation, and chemical pre-treatments.

Work during this report period concentrated on the understanding of the water vapor/ O_2 -grown oxide and on means to depth-profile the layer without modifying its chemical composition.

One of the most promising techniques for studying thin oxides involves depth profiling. Other researchers have reported such studies, typically using Ar-ion bombardment as a means of milling the oxide surface. Our recent results, as well as those of other workers in the field, have demonstrated that such bombardment with high energy ions (> 1 KeV) affects the chemical composition of the oxides. We have, therefore, concentrated on developing a technology for wet chemical etching of oxide films in a manner that is both extremely controllable and does not alter the oxide composition.

Results to date in this effort demonstrate the feasibility of this wet chemical etch approach to profiling. In the following, results will be given which illustrate the controllability of the technique, allowing one to remove 5-7 Å of the oxide per etching step.

The key to controlling a wet chemical etch is to control the exposure time of the sample to the etching solution. This is done using a spinner technique, which involves rotating the sample rapidly, while dropping a minute reproducible amount of etchant on the sample. Exact control over the etch rate can be maintained by varying the rate at which the sample is spinning and the amount of etchant added.

Initial experiments utilized GaAs with 30Å-thick oxide grown in H_2O -saturated O_2 at room temperature. A 0.1% Br_2 /methanol solution was used as the etchant. Six sequential etches were performed, using XPS to monitor surface composition between etches.

The As 3d region is shown in Figure 11. The Z axis represents the sequential etches plotted in such a way that one is looking from the initial oxide surface

toward the oxide/substrate interface. The Z axis represents a coordinate that is proportional to the oxide thickness. Absolute calibration of this thickness relationship is now being undertaken. The peak 3.2 eV higher in energy than the substrate line is known from this work to be arsenic (III) oxide. After five sequential etches it can be seen that the oxide has been completely removed, implying that approximately 5-7Å are removed per etch. The As 3d line due to the substrate can also be seen to increase as the etching proceeds, as anticipated. Efforts are underway to see if this increase in substrate signal is consistent with the signal attenuation through the oxide. Such information will yield information regarding oxide uniformity; i.e., whether the oxide is indeed uniform or if it is composed of oxide islands or areas of varying thickness (Ref. 8). It will also confront the possibility suggested by SiO₂-related studies in this laboratory, that the electron attenuation coefficient is a function of oxide thickness, rather than constant as is normally assumed.

Figure 11. Depth Profile of GaAs Oxide Grown by Water Vapor/Oxygen Exposure at Room Temperature Looking Into the Oxide From the Surface. Chemical Etchant is 0.1% Bromine in Methanol.

Figure 12 shows this same data on an expanded y axis and plotted such that one is looking from the oxide interface toward the initial surface. The expanded scale shows the smoothly decreasing oxide intensity. Further scale expansion suggests an increase in intensity in the region 4.5 eV (arsenic (IV) oxide) higher in energy than that of the substrate relative to the oxide peak at 3.2 eV. Thus, the oxide appears to become quite complex as one nears the interface. Work is underway to determine the exact chemical nature of these spectral changes.

Figure 12. Depth Profile of GaAs Oxide Grown by Water/Vapor Oxygen Exposure at Room Temperature Looking Into the Oxide from the GaAs. Chemical Etchant is 0.1% Bromine in Methanol.

Figure 13 shows the gallium region for the same set of etches. The data is plotted such that one is looking from the initial surface toward the oxide/substrate interface. Again note the apparent uniformity of the etch. The gallium oxide peaks fall 1.1 eV and 1.4 eV higher in energy than the substrate peak and, thus, both appear unresolved as a shoulder on the main peak. On-going efforts involve not only quantification of the intensity as discussed earlier, but also, mathematical deconvolution of the peaks to determine the exact contributions of

the two gallium oxides at the various oxide thicknesses.

Figure 13. Same as Figure 11 but for Ga3d region.

In addition to a higher than expected intensity in the As 3d region between the oxide and substrate peaks, the substrate peak in Figures 11 and 12 shows the As $3d_{3/2}$: As $3d_{5/2}$ intensity ratio to be 5:6. One would theoretically expect this ratio to be 2:3. It has been suggested by this laboratory and by other researchers (Refs. 1,9) that these anomalous intensities can be accounted for by the presence of arsenic metal occurring 0.9 eV above the substrate binding energy. In an attempt to verify the presence of the free metal, an estimate of the As 3d doublet was obtained, using an iterative procedure. This 2:3 doublet was scaled appropriately to the experimentally-obtained As 3d doublet and subtracted. The result was a small doublet 0.6 eV upfield, corresponding to arsenic metal. Figure 14 indicates the results from each sequential etch. Note that the intensity of the arsenic metal peak increases as one approaches the interface. There are two possible explanations for this: (1) The arsenic metal has accumulated as a discrete layer at the interface. The change in intensity is then simply a result of electron attenuation through the oxide. (2) There exists a concentration gradient

of arsenic metal which increases in the direction of the interface. One can distinguish between these two explanations by quantifying the spectra. This effort is currently underway and should prove to be extremely important in understanding solar cell characteristics since such an arsenic layer could very well control the GaAs surface potential. There is also the possibility that another arsenic species is present since the resulting arsenic metal doublet is not of a 2:3 intensity ratio.

Figure 14. As 3d Difference Spectra for Six Etch Steps Starting From 0 (Surface) to 6 (Interface).

The oxygen 1s line for the series of etches is shown in figure 15. The profile is displayed as a contour plot. The Y axis represents the sequential etches and is, therefore, proportional to oxide thickness. The data are plotted such that one is looking from the initial oxide surface (etch #0) toward the interface (etch #6). The contour lines are lines of equal intensity. One should note the shift of the oxygen 1s line toward higher binding energy as the interface is approached. This appears to be a continuous rather than abrupt shift from 531.2 to 532.0 eV. This shift is probably due to the bromine from the etch solution reacting with the oxide. Concurrent with the oxygen 1s shift, one finds

an interesting Br 3d signal (see figure 16). Such shifts demonstrate the sensitivity of the profiling technique to small chemical changes in the oxide.

Figure 15. Contour Plot of the Oxygen 1s (See Text).

Figure 16. ESCA Scans Showing Br, As (Bonded to Oxygen), As (GaAs Substrate), Ga (Bonded to Oxygen) and Ga (GaAs Substrate) Peaks for Different Bromine/Ethanol Etch Steps.

In addition, mathematical deconvolution of the oxygen 1s signal from oxidized GaAs which has not been etched with bromine/methanol shows the presence of two species of oxygen at 530.7 and 531.9 eV. These are probably due to the various As and Ga oxides present. Efforts are underway to understand how these shifts relate to the oxide composition as a function of oxide depth.

Although the bromine/methanol etch has served as a means of developing the spinning procedure for wet chemical etching of GaAs oxides and demonstrating the controllability of the method, it clearly modifies the oxide chemistry. Thus, a second etch using HCl and ethanol in a ratio of 1:10,000 is currently under development. Thus far, no reaction of this etch with the oxide has been detectable. It promises the desirable characteristics--controllability and no alteration of the oxide. Initial results indicate that only a few angstroms per etch can be removed. This profiling technique combined with mathematical deconvolution of the XPS promises to help considerably in understanding the complex chemical nature of semiconductor oxides and their interfaces.

E. Surface State Electric Characterization

Since the large enhancement of V_{oc} obtained by the introduction of an interfacial layer is most likely caused by modification of the surface states normally obtained by the application of metal contacts to the GaAs surface, a way of detecting and characterizing these states by electrical means is highly desirable. Several alternative methods are being considered.

Preliminary measurements on test structures will be used to evaluate the magnitude of some key parameters and time constants associated with the interfacial oxide layer. The test structures are 1- and 5-mm circles of 100Å-thick gold, evaporated on the oxidized GaAs. Depending on the typical magnitudes of the parameters, the following methods are being investigated.

1. High-Low (Frequency) Method

With this technique, the determination of interface states density is made possible by comparing the low-frequency MOS capacitance with the MOS capacitance at a frequency high enough so that surface states have no contribution to the measured capacitance. This high-frequency (HF) limit may be difficult to obtain

because the thin oxide layer of the device is highly conductive (a desirable property as far as the solar-cell operation is concerned), making the time constant associated with the surface states very small. As a result, the required frequency for the HF measurements is prohibitively high. These considerations may make it necessary to grow somewhat thicker oxides or to go to lower measurement temperatures for these specific measurements. The low frequency capacitance can be calculated from slow charge-voltage measurements using a coulombmeter.

The above measurements in conjunction with the knowledge of doping and surface potential should give one enough information to get the interface state density and oxide capacitance.

2. Fast and Slow Charge-Voltage Measurements

Here, the slow charge-voltage measurement is made to get the low-frequency capacitance as before, but instead of trying to make a high-frequency measurement that excludes the effect of surface states completely, a faster charge-voltage measurement is made so that the effects of finite time constant associated with surface states become measurable. This method is limited by the speed of the charge-measurement circuitry. Combining this information with an independent measurement of the effective oxide resistance, doping profile, and surface potential makes it possible to calculate the desired parameters.

3. AC Measurements (Capacitance-Conductance)

It may also be possible to employ a simplified conductance technique. The disadvantage of this technique is that it does not lend itself to automation without a major undertaking in setting up the digital measurement system and required controls. Therefore, this method, if used, would not be a routine part of our investigation; rather it could provide means for an independent check on results obtained through other tests.

4. Temperature Dependence

A somewhat different approach is afforded by the temperature dependence of the Fermi level in the semiconductor. Variation of barrier heights at different temperatures can give information to deduce some parameters of interest. The

success of this method depends on how accurately the barrier heights can be measured. It is possible that a simple $1/C_2$ -vs- v plot would be adequate.

The doping level is made use of in the procedures outlined above. The determination of the doping profile in GaAs is made from capacitance-voltage characteristics of the device. Except for the ac capacitance-conductance measurement, the above methods can be carried out and analyzed in an existing automated digital-measurement facility at JPL. The most useful methods will be used to follow the effect of process and to correlate with chemical information and solar-cell parameters. Further details of the techniques which are determined to be useful with AMOS test structures will be given in future reports.

Preliminary results from the high-low (frequency) technique show that, for an oxide thickness of about 40Å, the high-frequency limit is reduced at around several hundred kHz. Thus, measurement of the capacitance at 1MHz should be satisfactory. Leakage currents have been too high to allow a reliable charge-voltage measurement with a consequent determination of the low-frequency capacitance. Both guard-ring structures and different surface preparations are being investigated in order to minimize the leakage currents.

F. Double Layer Schottky Barrier Solar Cell

The main factor of SB solar cells limiting the efficiency as compared to p/n junction solar cells made from the same semiconducting material is the open-circuit voltage. Thus, for example, good quality heteroface devices on single crystal GaAs exhibit values of V_{oc} between 0.9 and 1.0 volts, whereas SB cells on non-oxidized GaAs typically show values around 0.5 volts (Refs 1 and 2). As discussed above, certain oxide interfacial layers have increased V_{oc} to as much as 0.8 volts by causing an increase in Schottky barrier height from 0.9 eV (67% of E_g) to 1.15 eV (80% of E_g). Because of probable increased minority carrier (hole) injection from the front metal contact which would subtract from the short-circuit current and possibly lead to increased recombination in the depletion region, it is not likely that significantly larger increases in ϕ_B will be useful. (The barrier height to hole injection as measured from the valence band edge is equal to the band gap E_g minus ϕ_B , and thus, decreases in proportion to an increase in ϕ_B .)

Because of these considerations, further significant improvements in SB solar cell efficiencies must rely on a novel structure. One structure is a double layer Schottky barrier (DLSB) solar cell (Fig. 17) previously disclosed at JPL (Ref. 11). The novel feature is the presence of a very thin semiconducting layer with a band gap higher than that of the underlying layer. A Schottky barrier cell fabricated on the higher band-gap material will provide for a higher ϕ_B , and hence, V_{oc} . Normally, there will be a correspondingly lowered short-circuit current density (J_{sc}) because of the reduced absorption of sunlight at the longer wavelengths. However, if the top layer is kept thin enough so that most of the carriers generated in the bottom layer by the transmitted light can be collected at the front surface contact, the overall efficiency can be higher than that of the conventional SB solar cell*.

Figure 17. Physical Structure of a Double Layer SB Solar Cell
Using GaAs and Al(Ga)As as the Active Materials.

*The addition of an oxide interfacial layer could, in principle, give a further improvement in efficiency of the DLSB cell just as it does in the single layer cell.

The thickness of the top layer should be such that the built-in electric field caused by the Schottky barrier extends through the interface region between the two semiconducting layers. The field could greatly increase the transmission of minority carriers by field-assisted tunneling through the barrier caused by the mismatch in bandgaps. Figure 18 shows an energy band diagram of a proposed DLSB solar cell using GaAs and $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ as the photoactive semiconductors, but drawn with the top layer too thick for the field-aided collection of holes generated in the GaAs. This n/n heterojunction has a barrier in the valence band of 0.6eV—too large for thermal diffusion of holes over the barrier—necessitating a large electric field in that region. Detailed calculations of the optimum thickness of the $\text{Al}(\text{Ga})\text{As}$ layer have not been performed, but the thickness must be less than several thousand Angstroms.

Figure 18. Energy Band Diagram for Double Layer Schottky Barrier Solar Cell in the Dark.

The choice of $\text{Al}(\text{Ga})\text{As}$ was made because of the excellent lattice match with GaAs and ease of epitaxial growth on the underlying GaAs (single crystal or grains). The close lattice match leads to a density of recombination centers

at the interface which is undetectable by deep level transient capacitance (Ref. 12). This, in turn, should lead to a very low recombination velocity at the interface - further increasing the likelihood of hole transport through the heterojunction.

The choice of an approximately 40% Al concentration for the Al(Ga)As layer comes from several considerations: 1) layers with high Al concentration would more difficult to grow uniformly by CVD - the preferred growth technique, 2) high Al-bearing layers are less stable, 3) the added increase in band gap beyond the transition from direct gap to indirect gap is relatively small (< 0.15 eV), and 4) the increase in electron effective mass and subsequent increase in the Richardson constant when the conduction band minimum changes from (000) symmetry to (100) symmetry will cause an increase in J_0 , the reverse saturation current, and hence, a drop in V_{oc} , partially offsetting the additional small increase in ϕ_B .

The major technology development required to prove the feasibility of the DLSB solar cell is the growth of the Al(Ga)As layer with approximately 1000Å thickness and with the desired stoichiometry uniformly over larger areas. Given this success, preferably by the use of CVD technology for reasons of scaling up, there are experimental results obtained in this laboratory and elsewhere which indicate that the proposed structure can successfully attain improved solar cell efficiencies. These are discussed next.

On an earlier program supported by NASA, SB cells were developed at JPL for $\text{GaAs}_{1-x}\text{P}_x$ ternary compounds for purposes of converting laser beam energy at wavelengths in the visible region of the spectrum. Conversion efficiencies up to 25% were obtained with cells fabricated before the AMOS effect was discovered. The purpose of the higher band-gap semiconductor (readily purchased from manufacturers of light emitting diode material using CVD technology) was to minimize losses due to excess energy above the band-gap of the laser beam photons. For photons in the yellow-green to deep blue portion of the spectrum, a phosphorous concentration of $X = 0.45$, giving an energy of 2.0 eV for the direct band gap, was found to be optimum as expected. Schottky barriers made with gold were 1.3 eV in energy and values of V_{oc} of up to 1.1 volts were obtained as

shown in Fig. 19. Such values were somewhat enhanced from what one would normally expect (~ 0.9 volts) because of some unintentional residual oxide and because of the high light intensity. Nevertheless, these data show that the use of higher band gap ternary compounds will provide the expected high V_{oc} - even without the use of interfacial oxide layers.

Figure 19. Experimental Light I-V Characteristic of a Baseline Schottky Barrier Solar Cell Fabricated on $GaAs_xP_{1-x}$ Using High Intensity Monochromatic (Laser) Light.

The growth of ultra thin $Al(Ga)As$ layers as $GaAs$ by LPE was attempted at Stanford University on a cooperative program funded by the Cal Tech President's Fund in 1975. At that time, sub-micron layers of $AlGa_xAs_{1-x}$ could not be grown over large areas. However, gold Schottky barriers were made on crystals where a portion of the $Al(Ga)As$ layer had been chemically etched off step-wise and the relative spectral response measured. Figure 20 shows that the response from the $GaAs$ bottom layer, which was not measurable with the top layer thickness of $0.5 \mu m$, is increasing with decreasing thickness. Viable solar cell structures could not be fabricated at that time due to funding limitations. Subsequently,

on another program funded by NSF, processing was developed to routinely grow $\text{Al}_{0.44}\text{Ga}_{0.56}\text{As}$ layers as thin as 300Å (Ref. 13). More recently, other laboratories have demonstrated the capability of growing uniform sub-micron GaAs layers by LPE (Ref. 14) and CVD (Ref. 15).

Figure 20. Experimentally Measured Collection Efficiency of a Double Layer Schottky Barrier Device with Thickness (t) of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ Layer Varied by Chemical Etching.

The successful development of a DLSB solar cell on single crystal GaAs could lead to efficiencies of 20 - 22% for AML, allowing for an eventual V_{oc} of 1.3 volts, fill factor of 80%, and J_{sc} of 20 mA/cm^2 . The latter value assures that only 20% of the current that otherwise is collected in a GaAs single layer is lost by recombination at the $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ interface. The value of V_{oc} also assumes a modest increase in voltage by the use of an interfacial layer (about 0.3 volts). Since the growth of the ternary compound layer by CVD processing on successfully grown poly GaAs should be comparable in difficulty to growth on single crystal, thin-film efficiencies should show similar improvements in conversion efficiency - potentially 16 to 18%.

Another advantage of the use of a DLSB structure is the increased possibility of a more stable solar cell at a somewhat lower efficiency. If it should prove impossible to develop an inherently long term stable AMOS cell because of degradation at the oxide-GaAs interface with time at elevated temperatures, an unoxidized DLSB structure with a V_{oc} of near 1.0 volt (16% efficiency on single crystal) could well prove to be more stable, and hence, be more cost efficient using life cycle costing.

SECTION III

THIN-FILM POLYCRYSTALLINE GaAs SOLAR CELLS

A. Approach

The adaptation of the above discussed AMOS single crystal processing to low cost GaAs films is the ultimate goal of this research task. The approach which will be initially pursued has been described in Reference 1. Figure 1 shows the structure envisioned for the first generation solar cell. Although tungsten sheet is now being used for germanium (Ge) recrystallization studies (see III.C), parallel studies of coated low-carbon steel or possibly Kovar sheet are being undertaken, and some results will be presented in the next report.

The use of a conducting metal substrate is desirable in order to avoid problems with contacting and fragility; consequently, virtually all efforts are addressed to the above mentioned metals.

Evaporated grid contacts using shadow masking are not desirable for economic reasons; hence, the use of conducting transparent coatings over the SB metallization would be an important development. Such coatings are not being investigated at this time, however.

A discussion of the material availability and material cost was given in Reference 1 and will not be summarized here. The conceptual production line presented in Reference 1 should be modified somewhat in view of the apparent utility of evaporated interfacial layers. Figure 21 is a revised drawing of a potential process sequence for the thin-film AMOS solar cell. The CVD growth of GaAs may be an automated large batch process, using two large reactors with common power supply and pumps, or conceivably, a continuous process as shown. The evaporated grid contact could possibly be replaced by a low temperature indium tin oxide coating or silver printing process and the AR coating process could be a spray-on coating (Ref. 16) in place of the evaporative process for further cost reduction. It does not appear likely that a non-evaporative means of depositing the SB metal is possible because of the high control of metal thickness required for efficient light coupling into the GaAs.

Figure 21. Conceptual Thin-Film AMOS Solar Cell Production Line.

Eventual elimination of the Ge interlayer may be possible by directly recrystallizing a GaAs polycrystalline film previously deposited on some appropriate low cost substrate. This would reduce cell costs by at least 10¢/peak watt if comparable cell efficiencies can be obtained. The use of Ge films, however, should assure high cell efficiency by means of the large grains obtainable.

B. AMOS Solar Cell Fabrication on Bulk Polycrystalline GaAs

As an interim step before the development of AMOS solar cells on thin films of GaAs deposited on recrystallized Ge, an investigation of such cells on sliced wafers of bulk polycrystalline GaAs was conducted. In particular, gold SB devices on these wafers were studied by scanning electron microscopy using electron beam-induced currents (EBIC). Results, which showed only slight decreases in response near grain boundaries, were consistent with the high short-circuit current density obtained from the cells under illumination. These results, as

well as some preliminary AMOS solar cell results using ozone-generated and O_2 glow discharge oxide interfacial layers, were given in reference 1. Values of V_{oc} , though enhanced, were only in the 600 - 650 mV range.

With the improved surface preparations and the development of the Sb_2O_3 evaporated oxide layer, it was decided to repeat the experiments on the bulk polycrystalline wafers (which had an epitaxial layer grown by organo-metallic CVD at Rockwell International to improve the intra-grain diffusion length). Figure 22 shows the light I-V characteristics of two cells with area equal to 0.20 cm^2 . One cell made in a region where there were only a few grains gave results nearly equal to those obtained on single crystal GaAs (see Fig. 3). The second cell was fabricated in a region containing a large number of grains with average dimensions between 100 and 500 μm . One can see that the V_{oc} values are considerably higher than those found using the earlier oxide techniques, and that less than 100 mV reduction in V_{oc} is obtained compared to the near single crystal region of the wafer. The efficiency of the latter cell was 14%, as compared to 16.2% for the cell fabricated on the near single crystal region.

Figure 22. Light I-V Characteristics of AMOS Cells (Sb_2O_3 oxide Layers) Fabricated on Bulk Polycrystalline GaAs Wafers.

Although these results are encouraging in the sense that very poor characteristics might imply a major difficulty with polycrystalline thin films, the converse is not necessarily true. Even if the grain sizes of the CVD-grown GaAs on recrystallized Ge are in the same range (hundreds of micrometers), high efficiency can only come about if the intra-grain quality, such as in morphology, crystallography, doping concentration, minority carrier lifetimes, etc, is consistently good from grain to grain. The possibility also exists that the nature of the grain boundary (GB) will be different from that found in bulk poly GaAs. This could simply be due to the fact that the bulk poly GaAs had been chemically polished, whereas one would wish to avoid wet chemistry process steps for the thin-film cells for economic considerations, or it could be due to more fundamental differences related to the larger degree of angle of the GB in the deposited film.

Should the GB play a role in determining barrier height in that region of the surface influenced by the GB (a linear dimension proportional to the average grain size with a width of several micrometers), the reverse saturation current of the diode will be larger than if there is no GB. This assumes that the barrier height will be lower at the GB because of the high density of defects giving surface states closer to the middle of the band gap. The metal-semiconductor contact on GaAs usually pins the metal Fermi level, and hence, the barrier height measured from the conduction band edge, at about two-thirds of the band gap. The Fermi level is apparently pinned at a position much closer to the valence band edge by the presence of a suitable oxide layer-giving a barrier height equal to 80% of the band gap. This effect may not occur at the GB because of differences in the dangling bonds available for interaction with the interfacial layer.

An estimate of the reduction in V_{oc} obtained, should such a situation occur in CVD thin films of GaAs, can be made assuming that there is a finite difference in barrier height between the two regions - one surrounding the GB and the other the remaining unperturbed area. Also, it is necessary to assume that no additional surface states are present in one of the two regions which may cause a recombination current through the states, and hence, a different diode ideality factor (n). Figure 23 shows the result of such a calculation for two different

areas representing GB areas: 1) 5% assuming 5 mm-wide GB and average grain size of 200 μm square and 3) 1% assuming 5 μm -wide GB and average grain size of 1 mm square. The magnitude of the barrier height in either area does not matter - only the difference in ϕ_B between the "normal" area (oxidized GaAs area) and the GB area. Even if ϕ_B between the metal and the GB were to be equal to ϕ_B of unoxidized GaAs (~ 0.90 eV), the difference of 0.25 eV from that obtained on an oxidized surface would lead to a loss of 170 mV in V_{oc} at 300°K if the area taken up by grain boundaries is 5% of the total area (200 μm grains), and 130 mV for 1% of the total area (1 mm grains). For the chemically polished wafers of polycrystalline GaAs, at least, the fact that a difference of about 70 mV in V_{oc} was measured for average grain sizes of several hundred micrometers (Fig. 22), implies that the difference in barrier height between the GB and surrounding area is less than 0.25 eV - perhaps about 0.15 eV.

Figure 23. Influence of Defect - Modified Barrier Heights on V_{oc} , Assuming Similar Transport Kinetics in Both Areas (Equal Ideality Factors). The Sum Total of Defected Areas is Represented by A_2 and the Unaffected Area by A_1 .

C. Germanium Recrystallization

A key element in this program is the use of an intermediate layer of Ge between the GaAs film and low cost metal such as steel. The cost of the cell could be as much as 25% higher with the Ge layer on a unit area basis; but, because of the large grain sizes obtainable, the cell cost on a per watt basis may actually be cheaper because of potentially much higher efficiency. Also the development time of an efficient thin-film GaAs solar cell should be shorter in time with the use of a recrystallized Ge layer.

The apparatus used for recrystallizing evaporated Ge films by laser beam techniques was described in Reference 1. The technique uses a Nd/YAG continuous wave laser focused to either a scanning spot or to a thin line, with background heating supplied by a 1000-watt strip heater. In either case, a narrow zone of melted Ge is swept across the substrate by translating the substrate under the beam. The thermal gradients and lack of strong interface reaction leads to individual grains crystallizing up to millimeters in length with excellent surface smoothness. The Ge films prior to recrystallization on tungsten have a (111) preferred orientation - although not strongly so. Orientation after recrystallization seems to be more random. Initial experiments are being performed on the more expensive tungsten sheet in order to better understand the recrystallization process and to allow GaAs growth experiments to proceed as well. The tungsten surface is very favorable for wetting and bonding when a thin (several hundred Å) silicon interlayer is used. No problem with thermal expansion mismatch has been found with respect to delamination or blistering. The mismatch between tungsten and Ge (and GaAs) is about 0.2% at 950°C - the melting point of Ge, and 0.1% at 600°C - a potential temperature for GaAs growth by CVD.

An investigation of tungsten - coated low carbon steel as well as the use of other coatings on steel is being initiated and will be reported on in future reports. The thermal mismatch between steel and Ge is about 0.8% at 950°C and 0.5% at 600°C. The purpose of a coating on steel is the prevention of alloying between the Ge and iron. Also if tungsten, or perhaps molybdenum, should prove to be cost effective, such coatings are desirable for their wetting properties with Ge (prevention of balling).

Earlier runs using line-focused laser beams were not successful using relatively thick 10- μ m Ge films because of insufficient melting through the film perpendicular to the surface (Ref. 1). This caused partial exposure of fine polycrystalline Ge when chemically etched prior to GaAs growth. Consequently, the scanning of an approximately 1-mm spot was used during this reporting period. Figure 24 shows that the effect of the spot sweep speed (frequency of function generator driving the scanning mirror) is not large. However, increasing the speed did cause the grains to become somewhat larger and more elongated similar to those obtained with a focused line.

Figure 24. Effect of Scanning Frequency of Laser Spot on Grain Morphology of Recrystallized Ge.

The Ge films are highly n-type because of the use of Sb-doped Ge with resistivity of 0.01 ohm-cm for the evaporation source. This assures the absence of a reversed bias barrier at the GaAs-Ge interface.

Recrystallization experiments were attempted on a number of substrates besides tungsten - none of which were successful. The use of uncoated steel or

nickel - iron (Kovar) sheet is not possible because of iron - Ge alloying. Mullite sheet - a successful candidate for silicon dip-coating - provided no wetting for the Ge, causing excessive balling. Apparent wetting occurs with graphite as well as good bonding - at least on ground finish graphite (POCO DFP-1). However, when the Ge is laser melted, no apparent grain growth occurs as the surface finish appears to be too coarse (Figs. 25 and 26) - at least for the film thickness of 10 μm used. In an attempt to obtain less porous graphite surfaces, a proprietary carbon-coated^{*} graphite substrate was tried. However, the coating did not have uniform properties across the whole area leading to patchy Ge films.

Cursory attempts at passivating steel (low carbon) or Kovar sheet by nitriding, siliconizing and carbonizing showed potential for preventing Ge alloying, but proved difficult to maintain uniform characteristics over a large area. Also wettability between the Ge and treated surface was generally not favorable for the simple processing used. Later reports will describe results using commercially-treated steel surfaces - particularly tungsten-or molybdenum-coated surfaces.

When recrystallizing Ge on tungsten sheet, occasionally a cracked surface appears such as seen in Fig. 27. However, the "cracks" are due to an inadvertant thick oxide layer which had formed because of oxygen leakage into the forming gas atmosphere. Chemical etching removes the oxide layer.

Another problem concerning warping of the substrate was observed when using lower thermal conductivity substrates such as steel or Kovar. The warping is due to the high temperature gradients established when laser spot scanning across the surface. The effect should be minimized by using thicker steel (up to 20 or 25 mil thickness), much larger areas than the convenient 2.2 x 2.2 cm size used now, and/or by increasing the background heating and lowering the laser power density.

*Tylan Industries

Figure 25. SEM Photograph of Laser Melted Ge Film on POCO DFP-1 Graphite (Ground Finish).

Figure 26. High Magnification View of One Nodule Seen in Fig. 26.

Figure 27. SEM Photograph of Laser-Melted Ge Film on Tungsten Showing Cracked Oxide on Surface.

D. GaAs Growth on Germanium

The growth of a GaAs film of 2-to 3- μ m thickness over large areas is best done by chemical vapor deposition (CVD) techniques. The use of organo-metallic (OM) sources for Ga is preferred over halide transport of Ga because: (1) there is no HCl etching of low cost substrates nor of the Ge when Ge is used as an interlayer, (2) the ability to grow the ternary compound (AlGa)As for the double layer Schottky barrier structure or for the heteroface p/n junction structure, (3) the potential for lower growth temperatures - perhaps 500 - 600°C - causing less Ge autodoping by diffusion and allowing for more mismatch in thermal expansion between the GaAs and substrate and (4) the use of a single temperature zone providing simplicity and uniform distribution of dopants and uniform degree of stoichiometry. Present major disadvantages are the high cost of the sources due to a miniscule market and variable purity levels.

Since no growth facility exists presently at JPL, GaAs growth has been subcontracted to Rockwell International Electronics Research Division (Contract No. 954863). This work is a continuation of Contract No. 954585 performed under the earlier program with NSF (Reference 1). Most of the preliminary work on the latter contract involved growth on single crystal and sliced bulk polycrystalline Ge wafers. Delays in initiating the follow-on contract allowed only a few growth runs on laser recrystallized Ge toward the end of this reporting period (March 1, 1977 - August 30, 1977). In addition, two growth runs by OM - CVD were performed by Professor S. Ghandi at Rensselaer Polytechnic Institute. All four runs performed under similar growth conditions found to be optimum for epitaxial growth on (100) GaAs wafers gave similar results when gold Schottky barriers were fabricated on them - shorted or very leaky barriers. Such results may be due to highly doped or defect layers. Considerably more data and SEM photos of the films will be presented in the next report.

A CVD growth facility using OM sources is planned at JPL. This will allow for more immediate GaAs growth on Ge films subsequent to the Ge recrystallization minimizing contamination problems. Also, as described in Section II.F, development of the double layer SB solar cell can be initiated with the particular and important requirement of (AlGa)As layer thickness under 1000Å. The capability for growing GaAs layers in-house will also allow for oxide interfacial layer experiments on surfaces free from wet chemical processing - more relative to eventual production processing.

A horizontal reactor design will be used in the initial growth runs. The reactor, with a rectangular cross-section, will be designed to: 1) suppress gas phase reaction, 2) improve thickness uniformity, 3) increase material utilization, 4) minimize convective effects and backstreaming of particulate matter which may embed itself in the growth layer and 5) provide for large scale-up. The designs have been completed and initial growth runs should occur by March, 1978.

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APPENDIX A
RESEARCH CONTRIBUTORS

JPL

R. J. Stirn - Member of Technical Staff (Principal Investigator)
Y. C. M. Yeh - Senior Engineer
F. P. Ernest - Senior Engineering Assistant
W. A. Hermann - Engineering Associate
C. J. Wu - Academic Part Time
B. D. Lamberty - Academic Part Time
F. J. Grunthaner - Member of Technical Staff (ESCA)
P. J. Grunthaner - Engineer (ESCA)

Rockwell International, Electronics Research Center

R. P. Ruth - Staff Scientist
D. P. Daptkus - Group Leader
W. Simpson - Member of Technical Staff

APPENDIX B

EXTERNAL DISTRIBUTION LIST

Mr. Jack Adams
Eagle-Picher Industries, Inc.
P. O. Box 737
Quapaw, Oklahoma 74363

Prof. W. Alexander
North Carolina State Univ.
P. O. Box 5275
Raleigh, NC 27607

Dr. Richard L. Anderson
Department of Electrical and
Computer Engineering
Syracuse University
Syracuse, NY 13210

Dr. Wayne A. Anderson
Department of Electrical Engineering
Rutgers University
New Brunswick, NJ 08903

Dr. Charles E. Backus
College of Engineering Sciences
Arizona State University
Tempe, AZ 85281

Prof. J. Ballentyne
Cornell University
Department of Electrical Engineering
Ithica, NY 14850

Mr. Gregory B. Banthold
Manager, Technical Programs
ALCOA
1200 Ring Building
Washington, D.C. 20036

Dr. Allen M. Barnett
University of Delaware
Institute of Energy Conversion
Newark, DE 19711

Dr. Elliot Berman
Center for Energy Studies
Boston University
145 Bay State Road
Boston, MA 02215

Mr. Daniel Bernatowicz
M/S 302-1
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Dr. Charles J. Bishop
Solar Energy Research Institute
1536 Cole Boulevard
Golden, Colorado 80401

Dr. H. Richard Blieden
ARCO
New Business Venture Solar Project
515 S. Flower St.
Los Angeles, CA

Prof. Karl W. Boer
University of Delaware
Institute of Energy Conversion
Newark, DE 19711

Dr. Henry W. Brandhorst, Jr.
M/S 301-1
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, CA 44135

Mr. Clark Bright
Optical & Conductive Coatings Company
P. O. Box 3368
Walnut Creek, CA 94598

Mr. Bruce L. Bryson
ALCOA
Alcoa Building
Pittsburgh, PA 15219

Prof. R. H. Bube
Department of Materials Science
Stanford University
Stanford, CA 94305

Prof. E. J. Charlson
Electrical Engineering
University of Missouri
Columbia, MO 65201

Mr. William R. Cherry
Division of Solar Energy
Department of Energy
Washington, D.C. 20545

Prof. Ting L. Chu
Southern Methodist University
Electronic Sciences Center
Dallas, TX 75275

Mr. Alexander Coursier
Metallurgie Hoboken - Overpelt N.V.
2430 Olen
Belgium

Dr. Leon Crossman
Dow Corning Corporation
12334 Geddes Road
Hemlock, MI 48626

Mr. Denis J. Curtin
Comsat Laboratories
Linthicum Road
Clarksburg, MD 20731

Dr. P. D. Dapkus
Rockwell International
Electronics Research Division
3370 Miraloma Avenue
Anaheim, CA 92803

Dr. Ed DeMeo
Electric Power Research Institute
3412 Hillview Ave.
Palo Alto, CA 94304

Dr. Wolfgang Doerfler
Honeywell, Inc.
2600 Ridgeway Parkway, NE
Minneapolis, MN 55413

Dr. J. Eckert
Esso Research and Engineering Company
P. O. Box 51
Linden, NJ 07036

Mr. Everett Y. Eslick
Vice President
African Metals Corp.
123 William Street
New York, NY 10038

Dr. John C. Fan
Lincoln Laboratory
Lexington, MA 02173

Dr. P. H. Fang
Boston College
Chestnut Hill, MA 02167

Dr. Don Feucht (10 copies)
Adv. Materials R&D Branch
Division of Solar Energy
Department of Energy
Washington, D.C. 20545

Dr. Erwin Fischer - Colbrie
Lawrence Livermore Laboratory
P. O. Box 808
Livermore, CA 94551

Prof. Stephen Fonash
Engineering Sciences
Pennsylvania State University
University Park, PA 16802

Mr. John Furber
Office of Technology Assessment
U.S. Congress
Washington, D.C. 20510

Prof. Harry Gatos
Massachusetts Institute of Technology
R 13-4126
Cambridge, MA 02139

Prof. S. K. Ghandi
Division of Electrophysics
Rensselaer Polytechnic Institute
Troy, NY 12181

Dr. Peter D. Glaser
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, MA 02139

Mr. Paul Goldsmith
TRW Systems
1 Space Park
Redondo Beach, CA 90278

Dr. G. Haacke
Chemical Research Division
American Cyanamide Company
Stanford, CT 06904

Prof. Yoshihiro Hamakawa
Faculty of Engineering Science
Osaka University
Osaka, Japan

Dr. James Harris
Rockwell International Science Center
P. O. Box 1085
Thousand Oaks, CA 91360

Mr. Daryl E. Heiby
ALCOA
1145 Wilshire Blvd.
Los Angeles, CA 90017

Dr. Ernie Henninger
Department of Physics
De Pauw University
Green Castle, IN 46135

Dr. Lloyd O. Herwig
Division of Solar Energy
Department of Energy
Washington, D.C. 20545

Mr. Jerome E. Hogan
ALCOA
Alcoa Building
Pittsburgh, PA 15219

Dr. Harold J. Hovel
IBM Research Laboratory
Yorktown Heights, NY 10598

Dr. Lau Hsu
Space Division
M.S. SL-10
Rockwell International
12214 Lokewood Blvd.
Downey, CA 90241

Dr. James Hutchby
NASA Langley Research Center
M.S. 231-A
Hampton, VA 23365

Mr. Peter A. Iles
OCLI
15251 Don Julian Rd.
City of Industry, CA 91746

Dr. Larry James
Varian Central Research Labs, K-105
611 Hansen Way
Palo Alto, CA 94303

Mr. John Jordan
Photon Power, Inc.
1820 Mills Avenue
El Paso, TX 79901

Dr. Lawrence L. Kazmerski
Solar Energy Research Institute
1536 Cole Boulevard
Golden, CO 80401

Dr. Ron Knechtli
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, CA 90265

Dr. Henry Kressel
RCA Laboratories
David Sarnoff Research Center
Princeton, NJ 08540

Dr. S. L. Leonard
The Aerospace Corporation
P. O. Box 92957
Los Angeles, CA 90009

Dr. I. A. Lesk
Motorola, Inc.
Corporate Research Laboratory
4039 E. Raymond Street
Phoenix, AZ 85040

Dr. S. S. Li
Department of Electrical Engineering
University of Florida
Gainesville, FL 32601

Prof. Fred Lindholm
University of Florida
231 Benton Hall
Gainesville, FL 32611

Dr. Joseph Lindmayer
The Solarex Corporation
1335 Piccard Drive
Rockville, MD 20850

Dr. Joseph H. Loferski
Department of Engineering
Brown University
Providence, RI 02912

Mr. John Loria
Office of Energy Programs
Code NT
National Aeronautics and Space
Administration
Washington, D.C. 20546

Dr. Leonard M. Magid
Division of Solar Energy
Department of Energy
Washington, D.C. 20545

Dr. H. M. Manasevit
Rockwell International
Electronic Research Division
Anaheim, CA 92803

Dr. Herbert F. Matare
P. O. Box 49197
Los Angeles, CA 90049

Prof. Tom McGill
Engineering and Applied Science
California Institute of Technology
319 Steele
Pasadena, CA 91106

Mr. James McNelly
Litronix
19000 Homestead Rd.
Cupertino, CA 95044

Prof. Art Milnes
Electrical Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

Dr. A. I. Mlavsky
Tyco Laboratories, Inc.
Waltham, MA 02154

Dr. John B. Mooney
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. J. M. Morabito
Bell Telephone Laboratories
Allentown, PA 18103

Dr. Tapan Mukherjee
National Science Foundation
Washington, D. C. 20550

Mr. Robert D. Nashby
Technical Library Division 3141,
Sandia Laboratories
Albuquerque, NM 87115

Prof. Marc Nicolet
Engineering and Applied Science
California Institute of Technology
321 Steele
Pasadena, CA 91106

Prof. Welville B. Nowak
Dept. of Mechanical Engineering
Northeastern University
Boston, MA 02115

Prof. L. C. Olsen
Joint Center for Graduate Study
100 Sprout Road
Richland, WA 99352

Dr. Henry Oman
The Boeing Company
Box 3999
Seattle, WA 98124

Prof. G. Pearson
Solid State Electronics Laboratory
Stanford University
Stanford, CA 94305

Dr. M. B. Prince
Division of Solar Energy
Department of Energy
Washington, D. C. 20545

Ms. Patricia Prinz
American Trade & Finance Comp.
2001 Jefferson Davis Highway
Arlington, VA 22202

Dr. D. L. Pulfrey
Dept. of Electrical Engineering
University of British Columbia
Vancouver, B.C. Canada

Mr. E. L. Ralph
Hughes Spectralab
12500 Gladstone Avenue
Sylmar, CA 91342

Dr. Paul Rappaport
Solar Energy Research Institute
1536 Cole Boulevard
Golden, CO 80401

Mr. Duncan L. Reynard
Philco-Ford Corporation
WDL Laboratories, MS R26
3939 Fabian Way
Palo Alto, CA 94303

Dr. E. S. Rittner
COMSAT
Clarksburg, MD 20734

Dr. Ralph Ruth
Rockwell International
Electronic Research Division
3370 Miraloma Avenue
Anaheim, CA 92803

Prof. J. Samuels
Howard University
2400 Sixth Street NW
Washington, D.C. 20001

Dr. Don Schueler
Sandia Laboratory
Sandia Base
Albuquerque, NM 87115

Mr. Fred Shirland
Westinghouse Research Labs
Churchill Boro
Pittsburgh, PA 15235

Dr. Gabor A. Somorjai
Department of Chemistry
University of California-Berkeley
Berkeley, CA 94720

Dr. Dwain Spencer
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304

Dr. Richard Statler
Naval Research Laboratory
Code 6603D
Washington, D.C. 20375

Dr. Ed. Stofel
Hughes Aircraft
2913 Palm Avenue
Manhattan Beach, CA 90266

Prof. Dan Trivich
Dept. of Chemistry
Wayne State University
Detroit, MI 48202

Dr. Donald L. Trueblood
6 Frankfurt/Main
Holzhausenstrasse 25
West Germany

Dr. Gene Wakefield
Texas Instruments Inc.
13500 N. Central Expwy.
Dallas, TX 75222

Mr. Gilbert H. Walker
M/S 231A
NASA Langley Research Center
Hampton, VA 23365

Prof. Edward Wang
College of Engineering
Wayne State University
Detroit, MI 48202

Dr. Douglas M. Warschauer
Division of Solar Energy
Department of Energy
Washington, D.C. 20545

Dr. Irv Weinberg
NASA Lewis Research Center
M.S. 302-1
21000 Brook Park Road
Cleveland, OH 44135

Dr. Ron Wichner
Lawrence Livermore Laboratory
MS L156
P. O. Box 808
Livermore, CA 94550

Prof. C. W. Wilmsen
Department of Electrical Engineering
Colorado State University
Fort Collins, CO 80523

Mr. Joseph F. Wise
AFAPL/POE-2 Wright-Patterson AFB
Dayton, OH 45433

Dr. Horst Witzke
Optel Corporation
Box 2215
Princeton, NJ 08540

Prof. Martin Wolf
University of Pennsylvania
113 Towne Building
Philadelphia, PA 19104

Dr. J. Woodall
IBM Research Laboratory
Yorktown Heights, NY 10598

Dr. Solomon Zwerdling
N.E. Solar Energy Center
70 Memorial Drive
Cambridge, MA 02142