360
0-22-80

MASTER

1953

DSE-4042-T7

DEVELOPMENT OF POLYCRYSTAL GaAs SOLAR CELLS

Quarterly Technical Progress Report No. 2 for May 1—July 31, 1979

By

D. L. Miller

Marshall J. Cohen

J. S. Harris, Jr.

Joseph Ballantyne

Alfred Hoyte

Elias Stefanakos

September 1979

Work Performed Under Contract No. EG-77-C-01-4042

Solar Energy Research Institute
Golden, Colorado

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$7.00
Microfiche \$3.50

September, 1979

DEVELOPMENT OF POLYCRYSTAL GaAs SOLAR CELLS

Quarterly Technical Progress Report No. 2
for period 05/01/79 through 07/31/79

By

D. L. Miller, Marshall J. Cohen and J. S. Harris, Jr.
Rockwell International Electronics Research Center
Thousand Oaks, California 91360

Joseph Ballantyne
Cornell University
Ithaca, New York 14853

Alfred Hoyte
Howard University
Washington, D.C. 20059

Elias Stefanakos
North Carolina A & T State University
Greensboro, North Carolina 27411

For

Solar Energy Research Institute
1536 Cole Blvd.
Golden, CO 80401

Prepared under Contract No. XS-9-8032-1

Approved by:

J. S. Harris
Program Manager

TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION.....	1
2.0 MATERIALS DEVELOPMENT.....	2
2.1 MBE Growths.....	2
2.2 CCLPE Growth.....	4
2.3 SIMS Characterization.....	5
3.0 INVESTIGATIONS OF GRAIN BOUNDARIES.....	13
3.1 Electronic Properties and Junction Formation in Small Grain Polycrystal GaAs.....	13
3.2 SLM Characterization of Polycrystal GaAs.....	16
3.3 Grain Boundary Resistance in GaAs.....	18
3.3.1 Theory.....	18
3.3.2 Experiment.....	23
3.4 Passivation of Grain Boundaries by Impurity Diffusion...	26
3.5 Grain Boundary Characterization.....	29
4.0 POLYCRYSTAL SOLAR CELL DEVELOPMENT.....	35
4.1 Schottky Barrier Solar Cells on Small Grain Poly- crystal GaAs.....	35
4.2 Modeling.....	37
4.3 MIS Solar Cells.....	41
4.3.1 Growth of Epitaxial Layers.....	41
4.3.2 The "Spin-on" Oxide Approach.....	44
4.3.3 Electrolytic Etching of Grain Boundaries.....	45
4.3.4 Polycrystalline Solar Cells.....	46
4.3.5 Stability of MIS Solar Cells.....	46
5.0 CHARACTERIZATION TECHNIQUES FOR POLYCRYSTAL MATERIALS.....	51
5.1 Routine GaAs Layer Characterization.....	51
5.2 Electron Beam Induced Current.....	53
5.3 Secondary Ion Mass Spectrometry (SIMS).....	54
5.4 Deep Level Transient Spectroscopy.....	56
5.5 Photo-Induced Transient Spectroscopy.....	57
5.6 Scanning Light Microscopy (SLM).....	59

TABLE OF CONTENTS (Cont.)

	<u>Page</u>
5.7 Scanning Auger Potential Profiling.....	60
5.8 Schottky Barrier Dark I-V as a Function of Temperature...	62
5.9 Photoresponse.....	64
6.0 REFERENCES.....	66

LIST OF FIGURES

	<u>Page</u>
1. SEM analysis of CCLPE growth of GaAs on Mo substrate (CC 050179 U). (a) SEM micrograph, (b) EDAX spectrum.....	7
2. SEM analysis of CCLPE growth of GaAs on Mo substrate (CC 050279 U). (a) SEM micrograph, (b) EDAX spectrum.....	8
3. Zn profile of solar cell #1862.....	10
4. As and Mo profiles of MBA-237 indicating abrupt interface between GaAs layer and Mo substrate.....	11
5. (a) MBA-265, (b) MBA-295.....	14
6. Dark I-V characteristics of MBA-265 (dashed lines) and MBA-295 (solid lines).....	15
7. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{10}/\text{cm}^2$..	20
8. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{11}/\text{cm}^2$..	21
9. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{12}/\text{cm}^2$..	22
10. Experimental determination of the activation energy versus inverse temperature for a single bad grain boundary in three GaAs polycrystalline samples: (a) $N_D = 8 \times 10^{15}/\text{cm}^3$, (b) $N_D =$ $8 \times 10^{15}/\text{cm}^3$, and (c) $N_D = 9 \times 10^{16}/\text{cm}^3$	24

LIST OF FIGURES (Cont.)

	<u>Page</u>
11. Band bending $e\phi_b$ as a function of donor density N_D for the interface density of states: $\sigma_1 = 1 \times 10^{12}/\text{cm}^2$ (at $E_1 = .41\text{eV}$) and $\sigma_2 = 1.9 \times 10^{12}/\text{cm}^2$ (at $E_2 = .90\text{eV}$).....	25
12. (a) IR-CL micrograph of grain boundary (200X) and (b) IR-CL intensity line scan (200X).....	30
13. (a) Secondary electron micrograph grain boundary (200X) and (b) IR-CL micrograph of grain boundary as shown in (a).....	31
14. Optical micrograph (500X) of a low angle grain boundary. The tetrahedral etch pits reveal the dislocation density along the grain boundary interface.....	33
15. AM1 I-V characteristics of Schottky barrier solar cell fabricated from MBA-265.....	36
16. Band bending $e\phi_b$ at a grain boundary.....	38
17. Band bending $e\phi_b$ as a function of donor density N_D and interface density of states σ_0 at $T = 300^\circ\text{K}$. Point defects assumed.....	40
18. Band bending $e\phi_b$ as a function of donor density N_D and interface density of states σ_0 at $T = 300^\circ\text{K}$. Dislocation produced defects assumed.....	42
19. Photovoltaic characteristics of the best of the cells made by electrolytically etched polycrystalline substrate.....	47

LIST OF FIGURES (Cont.)

	<u>Page</u>
20. Grain boundaries in unetched part of wafer (Mag = 200X).....	48
21. Surface of negatively electrolytically etched grain boundaries, note increase in boundary width (Mag = 200X).....	49
22. Electrolytically etched grain boundaries (GaAs) with microscope focused on the bottom of the grain boundary (Mag = 200X).....	50

ABSTRACT

Investigation of grain boundaries in GaAs, growth of small-grained GaAs, and solar cell fabrication on small-grained material continued this quarter. Some highlights were the fabrication of MS cells of small-grained GaAs grown on Mo, the fabrication of MIS cells using spin-on oxides, and the determination of interface state density at a high-resistance grain boundary. Initial measurements show that series resistance and shunt leakage seriously degrade the performance of cells made from small-grain polycrystal MBE GaAs, leading to efficiencies less than 1%.

1.0 INTRODUCTION

Progress in the development of high efficiency single crystal GaAs solar cells has been phenomenal over the past three years. Over this period, GaAs cell efficiencies have gone from 16% up to nearly 25%, the highest value for any solar cell, and approaching the theoretical limit for a single cell structure. Numerous systems studies of various solar cell options suggest that the lowest, long term solar electric generating costs will be achieved by very low cost, polycrystal or amorphous thin film devices. The successful reduction of the adverse effects of grain boundaries could lead to polycrystal solar cells with efficiencies of more than 15%. The realization of 10% conversion efficiency in a thin film polycrystal structure is the goal of this program.

In this report, we discuss our progress during the past quarter in a number of areas. Efforts have continued to optimize the growth of GaAs by MBE on low cost conducting substrates. Measurements were made to correlate the electronic properties with the growth conditions of polycrystal GaAs and we have begun to fabricate solar cells on this material. At Howard University, work has progressed toward developing stable spin-on oxides for use in MIS solar cells and at NCA&TSU the results of theoretical calculations have been used to analyze experimental data.

In section 5.0, we describe the various measurement techniques that have either been developed under or utilized during this program. The principles of the experiments, the ease of sample preparation and measurement execution as well as the solar cell and materials parameters that are determined are all summarized.

2.0 MATERIALS DEVELOPMENT

Materials growth at the participating institutions has been aimed at two goals. The first is to provide a continuing supply of material for the development of new solar cell structures and fabrication and characterization projects; the second is to develop a technique to grow relatively large grained thin film polycrystal GaAs on foreign substrates.

2.1 MBE Growths

(Rockwell International Electronics Research Center)

GaAs was grown by MBE on self-supporting ultra-thin (600-1000Å) carbon films to use in studies of nucleation and the initial stages of growth of GaAs on graphite. Self-supporting carbon films were used since previous work on layers greater than 200Å thick had shown that nucleation and growth were essentially identical on several types of graphite and carbon coated graphite.

SEM and TEM studies of GaAs layers 25-200Å thick showed that the layers grow initially by the coalescence of very small (<100Å diameter) mobile crystallites. These crystallites generally contain one or more grain boundaries and the layers formed by their coalescence contain a very large number of grain boundaries in the volume adjacent to the substrate. In addition, no preferred orientation is observed for the isolated crystallites in contrast to the high degree of preferred orientation observed for thick (2μm) layers. This suggests that the preferred (111) grain orientation in thicker layers grown on graphite arises from the dominance of (111) grains during

the layer growth rather than the coalescence of similarly (111) oriented nuclei. This conclusion is by no means certain, however, since growth on the self-supported carbon films occurred at reduced substrate temperature due to poor thermal contact inherent in the mounting arrangement. Since preferred orientation in thicker layers is a strong function of substrate temperature, the reduced temperature during these growths may have been sufficient to change the nature of the nucleation.

In addition to growth on carbon films, GaAs was grown on vitreous carbon, molybdenum and carbon coated-molybdenum. Growth on vitreous carbon was very poor with extremely small crystallite size. Since the carbon sample degassed at high rates throughout the layer deposition (despite previous attempts to bake it out), the poor morphology may have been the result of contamination. A $2\mu\text{m}$ thick GaAs layer grown on a molybdenum substrate coated with evaporated carbon ($\sim 2000\text{\AA}$) consisted of hillocks approximately $3\mu\text{m}$ across which were composed of a large number of very small ($0.1\text{--}0.5\mu\text{m}$) grains. This morphology was unexpected and is not yet understood.

A GaAs layer was also grown on a polycrystal aluminum substrate using an electropolishing bath designed to reduce the sputtering time necessary to produce a clean surface. $2000\text{\AA}$ of aluminum was deposited on the sputter cleaned bulk aluminum substrate in the MBE chamber and was then reacted with arsenic at 600°C . GaAs was then deposited over this AlAs layer. The resulting layer was small grained ($\sim 1\mu\text{m}$) with what appeared to be chunks of material lying on the surface. More work needs to be done to adequately assess this technique.

In the latter part of the quarter, a number of GaAs small grained polycrystal layers were deposited on molybdenum substrates in order to duplicate and improve on earlier results where encouragingly small shunt currents were obtained in dark I-V measurements (layer MBA 265; see Section 3.1). The main difficulty identified in these I-V measurements was a high series resistance. Based on studies of series resistance as a function of doping and substrate material type, the cause of the series resistance was tentatively identified to be the result of the small grained GaAs itself, rather than contacts to the substrate material.

2.2 CCLPE Growth

(North Carolina A&T State University)

This quarter's efforts were focused on the growth of GaAs on molybdenum substrates. A molybdenum sheet (0.25mm thick) was sheared to the required substrate dimensions and was cleaned and then briefly etched ($2\text{H}_2\text{O}_2 + \text{NH}_4\text{OH} + 7\text{H}_4\text{O}$). The molybdenum substrates were coated on the back surface with Ga to insure a uniform electrical contact over the entire area. Two of these growths were sent to Rockwell for SEM and EDAX analysis. The following are the CCLPE growth conditions for these two samples:

<u>Sample</u>	<u>CC050179U</u>	<u>CL050279U</u>
Growth Temperature	750° C	750° C
Current Density	20A/cm ²	20A/cm ²
Growth Time	10 min.	30 min.

The Ga melt was saturated with GaAs at 750°C before growth.

Figure 1a is a scanning electron micrograph of an area of sample CC050179U. This area has grains of up to 10 μ m in diameter. The corresponding EDAX data for the large grain (labelled x) is shown in Fig. 1b. No quantitative analysis of the constituents was available. The channels associated with the x-ray spectra of Ga, As and Mo are shown in Table 1.

In Fig. 1b, the Mo-L $_{\alpha}$ and Mo-K $_{\alpha}$ lines are readily detected, as well as the Ga-L $_{\alpha}$, Ga-K $_{\alpha}$ and Ga-K $_{\beta}$ lines. The As peaks appear quite low; however, a quantitative analysis would be required to determine whether it is present in a significant amount.

The SEM and EDAX results from sample CC050279U are shown in Figs. 2a and 2b. A second type of crystallite configuration -- filamentary -- is apparent. This same crystallite structure is observed on the back surface of the sample after growth. This presumably is a result of the dissolution of the Mo substrate by the Ga contact film and subsequent regrowth of Mo or a Mo-Ga compound. The EDAX area scan for this sample is similar to CC050179U, i.e., large Ga and Mo peaks and weak As lines.

2.3 SIMS Characterization (Cornell University)

Work on the SIMS characterization of solar cell materials during this quarter included impurity analysis of three GaAs samples and profiling of two solar cell structures. Several experiments into molecular detection for improving sensitivity gave promising results.

TABLE 1: X-ray Spectra of Ga, As and Mo Channel

	K_{α}	K_{β}	L_{α}	L_{β}
Ga	9.241	10.262	1.098	----
As	10.524	11.722	1.282	----
Mo	17.441	19.599	2.293	2.394

(a)

(b)

Fig. 1 SEM analysis of CCLPE growth of GaAs on Mo substrate (CC 050179 U). (a) SEM micrograph. (b) EDAX spectrum.

(a)

(b)

Fig. 2 SEM analysis of CCLPE growth of GaAs on Mo substrate (CC 050279 U). (a) SEM micrograph. (b) EDAX spectrum.

Rockwell samples 1826 and 1828 and Morgan substrate material were mass analyzed for impurities. These materials were clean except for signals from the highly sensitive Na^+ , K^+ , Al^+ , Cl^- and Br^- . The nominal doping, $n \cong 10^{18} \text{cm}^{-3}$ Te in the substrate, is a detectable level for Te^- in GaAs.

Solar cell #1862 was profiled for AlGaAs composition and layer thickness. The surface, however, was too rough to allow resolution of the 500Å of 1.5μm layers. The intentional Zn impurity was detected and ^{64}Zn was profiled. An anomaly which may correspond to the surface layer-second layer interface was seen (Fig. 3); again, the extreme surface irregularity made the depth of this feature indeterminate. Impurities similar to the above samples were also seen.

Sample MBA-237 was profiled for Ga^+ , Mo^+ and As^+ to assess the GaAs-Mo interface. Figure 4 shows the As^+/Mo^+ profile of the sample. The interface was measured at 2000Å, with the SIMS tuned to moderate deep resolution to achieve a good As^+ signal. At this resolution, such a sharp interface tends to indicate little if any diffusion between the layers, and similarly indicates no compound formation at the interface. Impurity mass analysis of the GaAs layer showed the usual alkali and halide impurities as well as a small amount of Cu^+ . The Mo layer contained only the K^+ , Na^+ , Cl^- and Br^- signals (Al^+ present was assumed to be an artifact of the GaAs surface layer as Ga^+ and As^- were also seen in the Mo spectrum).

During the quarter, work continued on improving the detection of elements important to solar cell studies by the use of molecular ions. Several

Fig. 3. Zn profile of solar cell #1862.

Fig. 4. As and Mo profiles of MBA-237 indicating abrupt interface between GaAs layer and Mo substrate.

triply bonded (isoelectronic with CN^-) species were studied in implanted semiconductor materials. All (group IV/group V) $^-$ species show signals greater than ten times the (group IV) $^-$ signal, and several show signals greater than the (group IV) $^+$ signal. For Sn in GaAs, however, the Sn^+ signal was comparable to the Sn As^- signal and the Sn^+ species should be used for Sn detection in GaAs. More implants are being profiled to produce a more complete list of the sensitivity of these molecular ions.

3.0 INVESTIGATIONS OF GRAIN BOUNDARIES

Investigations of grain boundaries are in progress at Rockwell, Cornell University and North Carolina A&T State University. Efforts include measurements to determine transport parameters in the vicinity of a grain boundary, junction formation in polycrystalline material, and attempts to identify and modify the chemical properties of grain boundaries.

3.1 Electronic Properties and Junction Formation in Small Grain Polycrystal GaAs

(Rockwell International Electronics Research Center)

Dark I-V measurements were made on gold Schottky barriers formed on a GaAs layer grown on a Mo substrate early in the quarter (MBA-265). The first $1.5\mu\text{m}$ had been doped very heavily ($\cong 5 \times 10^{18}\text{cm}^{-3}$) n-type with Sn, while the last $1\mu\text{m}$ of the total $2.5\mu\text{m}$ thickness was undoped ($n \cong 10^{17}\text{cm}^{-3}$ residual doping from MBE background). An electron micrograph of the layer is shown in Fig. 5a and the I-V data are plotted in Fig. 6.

This structure exhibited considerably less series resistance than previous small grain polycrystal material. The leakage current was also quite low. This is particularly encouraging, since the residual 10^{17}cm^{-3} doping is much larger than would be ideal for low leakage diodes. Earlier experiments on large grain polycrystal material showed large increases in leakage current as the doping increased from $5 \times 10^{15}\text{cm}^{-3}$ to $5 \times 10^{17}\text{cm}^{-3}$. If similar changes in leakage occur for small grained material, doping den-

(a)

(b)

Fig. 5 (a) MBA-265. (b) MBA-295.

Fig. 6. Dark I-V characteristics of MBA-265 (dashed lines) and MBA-295 (solid lines).

sities of 10^{16} cm^{-3} or below should lead to acceptably small shunt current in GaAs grown on molybdenum by MBE.

In an effort to improve on the electronic properties of MBA-265, the same structure was grown with the exception that a background of H_2 gas (not ionized) was emitted to the MBE chamber during the growth. The results (MBA-295) were not particularly encouraging. The grain size tended to be smaller than obtained with MBA-265 as can be seen in Fig. 5b. The dark I-V characteristics of these layers (Fig. 5) were all virtually identical to those seen for MBA-265, with relatively little scatter. This is surprising, since the grain size was roughly half that of MBA-265.

During this quarter, effort also went into setting up a computerized test facility. With the help of Earl Martin, a student at North Carolina A&T, we have automated the data acquisition and analysis of dark and illuminated I-V and C-V characteristics.

3.2 SLM Characterization of Polycrystal GaAs (Cornell University)

This quarter the emphasis of the SLM investigations has shifted from a study of the electronic properties of single grain boundaries to a study of (1) internal photoemission as a tool for measuring Schottky barrier height in Electronics Research Center Schottky dot specimens, (2) spatially

resolved photoluminescence as a probe of recombination at grain boundaries, and (3) reverse bias characteristics of transparent Schottky barriers under illumination to determine diffusion lengths in polycrystalline GaAs.

In regard to the first, preliminary measurements have been made on a Rockwell specimen using illumination by a Nd:YAG laser (1.06 μ m wavelength) on the back surface. A specimen holder allowing fast contacting to a specific Schottky dot was assembled. It was found that reasonable photocurrents could be obtained with the available light levels. By using a tuneable monochromatic source to vary photon energy, measurements of the barrier height should be possible.

A photoluminescence apparatus is in the process of being set up. A LN₂ cryostat for cooling the specimen is nearly ready.

Work has progressed toward developing a method for making spatially resolved minority carrier diffusion length measurements using semitransparent Schottky barriers under variable reverse bias. Good semitransparent Schottky barriers have been deposited by e-beam evaporation which are similar electrically to the barriers deposited in the MBE growth chamber at the Electronics Research Center. The method relies on varying the depletion depth by appropriate reverse bias, thereby changing the depletion depth relative to the penetration depth of the light and thus changing the amount of photocurrent collected at the barrier. Presently, measurements have been carried out at 603nm and 799nm, but have failed to exhibit any change in photocurrent as a function of bias. These investigations are continuing to discover the

source of this problem.

A method for determining grain orientations in large-grain polycrystalline GaAs has been developed. The method uses a multi-wire back-Laue x-ray detector operating in real time. This allows rapid orientations to be made. Grains as small as approximately 2mm can be measured and orientations are accurate to approximately 2 degrees. The orientations of a number of North Carolina A&T State University specimens were determined in this way.

3.3 Grain Boundary Resistance in GaAs (North Carolina A&T State University)

3.3.1 Theory

Majority carrier transport across a grain boundary of height ϕ_b' can occur due to two distinct mechanisms, thermionic emission over the barrier and tunneling through the barrier. For donor levels $N_D < 10^{18}/\text{cm}^3$, the tunneling contribution to the current is expected to be small. For a thermionic current to exist, only those carriers with energy greater than ϕ_b' can contribute to the current. The thermionic current which flows across the grain boundary when a potential V is applied can be written as

$$J = J_{th} = A^* T^2 \exp(-\phi_b/k_B T) [\exp(eV/k_B T) - 1]. \quad (1)$$

The exact form of A^* is not important in the following discussion provided that A^* is assumed temperature independent. For a voltage V such that

$eV \ll k_B T$, the barrier resistance can be written as

$$R_B = (k_B/eA^*) [\exp(\phi_b'/k_B T)/T], \quad (2)$$

where $R_B = V/J$ (ohm/cm²). Eq. 2 can be rewritten in the form

$$[k_B \partial \ln(TR_B)]/\partial(1/T) = \phi_b' - T(\partial \phi_b'/\partial T). \quad (3)$$

Using the relationship between barrier height ϕ_b' and band bending ϕ_b , that is

$$\phi_b' = \phi_b + r = \phi_b + kT \ln(N_c/N_D), \quad (4)$$

one obtains

$$[k_B \partial \ln(TR_B)]/\partial(1/T) = \phi_b - T(\partial \phi_b/\partial T). \quad (5)$$

If the band bending is weakly temperature dependent, i.e., $\partial \phi_b/\partial T \cong 0$, then the activation energy is equal to the band bending.

Figures 7-9 demonstrate that the temperature dependence of ϕ_b is a function of the interface density of states σ_0 . For $\sigma_0 = 10^{10}/\text{cm}^2$, ϕ_b is temperature independent. For $\sigma_0 = 10^{11}/\text{cm}^2$, ϕ_b is temperature dependent only at low donor levels, 10^{14} - $10^{15}/\text{cm}^2$. For $\sigma_0 \geq 10^{12}/\text{cm}^2$, ϕ_b is temperature dependent at all donor levels (except very high donor levels) but the tem-

Fig. 7. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{10}/\text{cm}^2$.

Fig. 8. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{11}/\text{cm}^2$.

Fig. 9. Band bending $e\phi_b$ as a function of temperature T and donor density N_D with an interface density of states $\sigma_0 = 10^{12}/\text{cm}^2$.

perature dependence is weak ($\Delta\phi \leq .2\text{eV}$ over a 400°K temperature range).

3.3.2 Experiment

Grain boundary resistance studies were conducted on long narrow bicrystalline samples (typical dimensions $.04\text{cm} \times .08\text{cm} \times 1.5\text{cm}$) cut from polycrystalline wafers such that a highly resistive (bad) grain boundary runs perpendicular to the long dimension of the sample. After cutting, the sample was cleaned, etched and tin contacts were alloyed to the sample. Curve tracer measurements were performed to verify the ohmic nature of the contacts. A constant current of $.01\mu\text{A}$ was passed along the long dimension of the sample and the voltage drop was measured as a function of T using a high input impedance voltmeter. Throughout the temperature range considered, the recorded voltage was $\leq 1\text{mV}$. The results are shown in Fig. 10 in the form of an activation energy versus inverse temperature.

The theory predicts a weak temperature dependence and this is verified by a straight line fit to the experimental points. Due to the weak temperature dependence of ϕ_b , the band bending ϕ_b can be equated to the slope of these lines (refer to Eq. 5). The data points of four samples are shown in Fig. 11. The solid line in the figure is a fit to the theory.

The solid theoretical curve was obtained using the self-consistent equation for band bending. The two dominant DLTS levels at $E_1 = .41\text{eV}$ and $E_2 = .90\text{eV}$ were used in the fitting. A preliminary best fit to the limited experimental data gives an interface density of states:

Figure 10. Experimental determination of the activation energy versus inverse temperature for a single bad grain boundary in three GaAs polycrystalline samples: (a) $N_D = 8 \times 10^{15}/\text{cm}^3$, (b) $N_D = 8 \times 10^{15}/\text{cm}^3$, (c) $N_D = 9 \times 10^{16}/\text{cm}^3$

Figure 11. Band bending $e\phi_b$ as a function of donor density N_D for the interface density of states: $\sigma_1 = 1.0 \times 10^{12} / \text{cm}^2$ (at $E_1 = .41 \text{ eV}$) and $\sigma_2 = 1.9 \times 10^{12} / \text{cm}^2$ (at $E_2 = .90 \text{ eV}$).

$$\sigma_1 = 1.0 \times 10^{12}/\text{cm}^2 \text{ at } E_1 = .41\text{eV (below } E_C)$$

$$\sigma_2 = 1.9 \times 10^{12}/\text{cm}^2 \text{ at } E_2 = .90\text{eV (below } E_C)$$

This is the first reported interface density of states per unit area for bad grain boundaries in GaAs. Additional experimental points are needed before a better fit can be obtained.

3.4 Passivation of Grain Boundaries by Impurity Diffusion (North Carolina A&T State University)

For the first few diffusion experiments potassium was chosen. It has a fairly large atomic radius so it would be expected to remain in position at the dislocation sites in the grain boundary. Also, its low melting point (64°C) makes it easier to work with than sodium.

A small amount of potassium was transferred in a nitrogen purged glove bag into a pyrex ampoule containing the GaAs sample. The ampoule was evacuated with a molecular sieve trapped mechanical pump and a sputter ion/sublimation vacuum pump. After sealing off the ampoule, it was heated in a small oven for the diffusion cycle.

Filamentary samples of polycrystalline GaAs which had been characterized by I-V vs. temperature measurements were chosen for the diffusion experiments. After characterization, the Sn contacts to the various grain regions were removed and the rectangular filament was etched in hot HCl to remove remnants of the Sn alloyed area. After the diffusion period, the Sn contacts were again applied (450°C, 2 min.).

In an early diffusion experiment, the GaAs filament was immersed in K at 140°C for several hours. The result was a complete dissolution of the GaAs in the K. Subsequent diffusions were performed with a small amount of K in the ampoule separated from the GaAs. The vapor pressure of K as a function of temperature is given in Table 2.

At a diffusion temperature of 180°C for six hours, the samples were badly pitted and crumbled easily during cleaning. Lowering the ampoule temperature to 140°C and diffusing for one hour resulted in samples with no visible surface deterioration. Preliminary I-V measurements on the polycrystal filaments indicated a slight increase in bulk resistance, possibly caused by the K acting as an acceptor and compensating a thin surface layer. (The polycrystal samples had bulk carrier concentrations in the 10^{16} cm^{-3} range). Further experiments with etching the surface to remove the bulk diffused K are in progress. It appears that the next experiments will involve a predeposition and drive-in diffusion sequence to saturate the grain boundary defects and minimize the bulk diffusion effect.

One of the difficulties in making the diffusion characterizations is the necessity of reapplying the Sn contacts after the diffusion. Since the diffusion temperature is relatively low, a characterized filamentary sample (I-V vs. temperature) will be diffused in potassium vapor without removing the Sn contact dots. If the Sn does not alloy drastically with the K, this process would greatly simplify the handling of the fragile filament and avoid the subsequent 450°C Sn alloy cycle.

TABLE 2: Vapor Pressure of K

Pressure (Torr)	Temperature (°C)
10^{-5}	91
10^{-4}	123
10^{-3}	161
10^{-2}	208

3.5 Grain Boundary Characterization (North Carolina A&T State University)

During this quarter we have reported the use of infrared cathodoluminescence (IR-CL) as an alternative technique to EBIC and SLM for differentiating the good from the bad grain boundaries. This IR-CL technique has an advantage in that no contacts to the sample are needed.

In the IR-CL technique, the electron beam is scanned across the region of observation. Among other effects, the 30KeV electrons striking the sample produce a non-equilibrium thermodynamic distribution of electrons in the conduction band. As the excited electrons decay, the process will in general be (1) radiative in the perfect crystal region or (2) nonradiative in the region of a defect. Thus, the absence of light serves to locate defect regions.

Figure 12a shows an IR-CL micrograph (200X) of a bad grain boundary. The grain boundary (strong dark line running diagonally) is very distinct due to nonradiative recombination at the defect states along the interface. Figure 12b shows the corresponding IR-CL intensity line scan of the same grain boundary. Note the reduction in the IR-CL signal in the grain boundary region.

A comparison between a secondary electron and an IR-CL micrograph of the same region shows excellent contrast between the grain boundary (i) and the grains. In addition, the IR-CL photomicrograph reveals a second grain boundary (ii) which is not evident in the secondary electron micrograph (see Fig. 13a).

Fig. 12(a) IR-CL micrograph of grain boundary (200X).

Fig. 12(b) IR-CL intensity line scan (200X).

Fig. 13(a) Secondary electron micrograph grain boundary (200X).

Fig. 13(b) IR-CL micrograph of grain boundary as shown in (a).

The IR-CL micrographs of "good" grain boundaries generally show little nonradiative (a small reduction in IR-CL intensity) while twins show only radiative recombination. "Bad" grain boundaries show strong nonradiative recombination characteristics and always appear as very dark regions.

Thus far all efforts toward understanding the electrical effects of polycrystalline GaAs have centered around understanding bad (highly resistive) grain boundaries. Perhaps of equal or greater importance may be the understanding of what makes some grain boundaries good. Using a combination of selective etchants and standard microscopy one good grain boundary was characterized.

A polycrystalline sample was cleaned by TCE, acetone, and then preserved in methanol. The sample was etched in Schell's Reagent composed of 1 part HNO_3 , 3 parts H_2O and .5% butylamine. The sample was etched for 15 minutes at room temperature, then rinsed in DI-water and dried immediately. An optical micrograph of a good grain boundary is shown in Fig. 14. In the intragrain regions we see a fairly uniform distribution of tetrahedral etch pits which are characteristic of dislocations in GaAs. In addition, the etchant has revealed microstructure of the good grain boundary. One can count the number of dislocations from which the grain boundary is comprised. The distance between the dislocation etch pits along the grain boundary is $\cong 1\mu\text{m}$.

From the simple Read theory, one would expect the space charge radius in this $N_D = 10^{16}/\text{cm}$ material to be $R \cong .1\mu\text{m}$. This indicates that the dislocation space charge cylinders do not overlap; this would mean that the grain boundary is very porous. A porosity in the grain boundary potential

10 μm

Fig. 14. Optical Micrograph (500X) of a low angle grain boundary. The tetrahedral etch pits reveal the dislocation density along the grain boundary interface.

would lead to a large drop in grain boundary resistance due to the fact that many majority carriers can transverse the grain boundary without the necessity of having to cross over a potential barrier.

4.0 POLYCRYSTAL SOLAR CELL DEVELOPMENT

The goal of this task is to develop solar cell structures which can be used with polycrystal materials.

4.1 Schottky Barrier Solar Cells on Small Grain Polycrystal GaAs (Rockwell International Electronics Research Center)

During this quarter we have begun the fabrication of solar cells on small grain polycrystal GaAs grown by MBE on potentially low cost substrates. Our first effort was with layer MBA-265, which was described in Section 2.1. Briefly, it consisted of a heavily doped ($5 \times 10^{18} \text{ cm}^{-3}$) layer of GaAs grown on electropolished molybdenum followed by a more lightly doped ($\cong 1 \times 10^{17} \text{ cm}^{-3}$) $1\mu\text{m}$ thick surface layer. A $50\text{\AA}$ thick semitransparent gold Schottky barrier was applied followed by a $2000\text{\AA}$ thick gold collecting grid.

The AM1 I-V curve is shown in Fig. 15. The results were disappointing and served mainly to illustrate the problems associated with polycrystal solar cells. The high resistivity of the material together with the low shunt resistance of the grain boundaries reduced all the relevant parameters and resulted in an efficiency $< 1\%$. One of the principal goals for the coming quarter is to improve on these results.

Fig. 15. AM1 I-V characteristics of Schottky barrier solar cell fabricated from MBA-265.

4.2 Modeling

(North Carolina A&T State University)

Due to the dangling or severely stretched bonds at a grain boundary interface, states are introduced deep into the band gap. The partial filling of these states by the donors in the grains adjacent to the boundary produces the band bending depicted in Fig. 16. Assuming that the excess charge donated to the interface is evenly distributed over the interface, Poisson's equation can be solved to obtain the depletion width, W , as a function of band bending, ϕ_b ,

$$W = \sqrt{8\epsilon_s \phi_b / eN_D} . \quad (6)$$

Invoking charge neutrality demands

$$WN_D = Q_s , \quad (7)$$

where N_D is the donor density and Q_s is the number of accumulated charges per unit area of planar interface. Using eqs. (6) and (7) we obtain

$$Q_s = \sqrt{8\epsilon_s N_D \phi_b / e} . \quad (8)$$

Another expression for Q_s can be obtained by integrating over the density of states $n(E)$ at the interface,

Fig. 16 Band bending $e\phi_b$ at a grain boundary

$$Q_C = \int_0^{E_C} n(E) f(E, E_F') dE \quad (9)$$

where $E_F' = E_F - e\phi_b$ (refer to Fig. 17) is the Fermi level at the interface, and $f(E, E_F')$ is the probability that the level at position E is filled.

Assuming Fermi - Dirac statistics, then

$$f(E, E_F') = \frac{1}{1 + \exp(E - E_F')} = \frac{1}{1 + \exp(E + e\phi_b - E_F)} \quad (10)$$

If a fraction r of the states are filled in the neutral condition, then the occupational probability should be modified to $(f(E, E_F') - r)$.

DLTS measurement on grain boundaries in GaAs at Cornell University suggest that the grain boundaries are dominated by two discrete flaw levels at $E_1 = .41\text{eV}$ and $E_2 = .90\text{eV}$ from the conduction band. Both flaw levels serve as electron traps and have equivalent volume densities of $N_1 > 1 \times 10^{16}/\text{cm}^3$ and $N_2 > 6 \times 10^{16}/\text{cm}^3$. These measurements indicate a density of states of the form,

$$n(E) = \sum_i \sigma_i \delta(E - E_i), \quad (11)$$

where σ_i is the number of flaw states per unit area of interface located at a position E_i . Substitution of Eq. (11) into (9) gives

$$Q_S = \sum_i \sigma_i f(E_i, E_F - e\phi_b). \quad (12)$$

Fig. 17. Band bending $e\phi_b$ as a function of donor density N_D and interface density of states σ_0 at $T = 300^\circ\text{K}$. Point defects assumed.

Equating Eqs. (8) and (12) yields the self-consistent equation for band bending,

$$\sum_i \sigma_i [f(E_i, E_F - e \phi_b) - r_i] = \sqrt{8\epsilon_s N_D \phi_b / e} \quad (13)$$

We have solved the self-consistent Eq. (13) using the data supplied via DLTS. The results are shown in Figs. 17 and 18. For the results shown in Fig. 15, the following parameters were used: $E_1 = .41$, $\sigma_i = \sigma_0$, $E_2 = .90$, $\sigma_2 = 6\sigma_0$, $r_1 = 0$ and $r_2 = 0$. The results shown in Fig. 16 use the same parameter values except $r_1 = .75$ and $r_2 = .25$. These r_1 and r_2 values would be characteristic of α and β dislocations, respectively.

The shape of the band bending ϕ_b curves versus donor density N_D is extremely sensitive to the interface density of flaw levels σ_0 . For low σ_0 ($\cong 10^{10}/\text{cm}^2$) the band bending decreases as N_D increases and becomes negligible at $N_D = 10^{16}/\text{cm}^3$. For high σ_0 ($\cong 10^{12}/\text{cm}^2$) the band bending first increases with increasing N_D , but drops sharply at high donor levels.

4.3 MIS Solar Cells (Howard University)

4.3.1 Growth of Epitaxial Layers

Numerous liquid phase epitaxial (LPE) GaAs layers were grown by using a horizontal sliding boat system. The layers were grown on n+ single crystal ($n \approx 6 \times 10^{17} \text{ cm}^{-3}$) as well as on n+ polycrystal GaAs substrates

Fig. 18. Band bending $e\phi_b$ as a function of donor density N_D and interface density of states σ_0 at $T = 300^\circ\text{K}$. Dislocation produced defects assumed.

($n \approx 2 \times 10^{18} \text{ cm}^{-3}$). The substrates were of dimensions 1.5 cm. x 1.5 cm. x 15 mils.

Before growth, the substrates were subjected to a thorough cleaning procedure. The lapped and polished sides of the wafer were gently scrubbed with Aquet using Q-tips followed by a mild ultrasonic agitation for about one minute. The wafer was then rinsed with D.I. water. Degreasing was initiated by electronic grade TCE from a spray bottle. Three displacive rinses followed by a mild ultrasonic agitation for at least one minute on the final rinse were executed. This step was repeated with acetone and methanol, respectively. The methanol was displaced by D.I. water while the latter was displaced by H_2SO_4 . The substrate was then soaked in H_2SO_4 while a 3:1:1 ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}:\text{H}_2\text{O}_2$) etch was prepared and kept at room temperature. The H_2SO_4 was poured off the substrate and replaced by the etch for approximately one minute, after which it was immediately quenched with D.I. water. The water was then displaced with HCl which was boiled for several minutes. Finally, the acid was displaced with methanol and then propanol. The wafer was kept in propanol until it was ready for loading into the furnace.

After having loaded the furnace, a vacuum pump was used to remove most of the air that rushed in during the loading process. By repeating the pumping cycle for about five times, 90% of the air would be removed. The remainder of the air was flushed out by using a high flow rate of hydrogen for about ten minutes.

The temperature of the furnace was raised to 715°C (T_0) and kept there for about 30 minutes, after which the cooling process was started.

With preassigned values of cooling rate (α) and amount of initial supercooling (ΔT) the temperature was lowered to $(T_0 - \Delta T)^\circ\text{C}$. At that time, the melt chamber containing an As-saturated Ga solution was pushed onto the recessed substrate. To terminate growth, the melt chamber was pushed off the substrate by means of a quartz push rod. The furnace was then cooled to room temperature and the substrate was removed. Excess Ga on the epilayer was removed by using methanol-soaked Q-tips.

The electrical properties of the epilayers grown on n+ single crystal GaAs substrates were investigated by Hall-van der Pauw measurements. For a typical $3\mu\text{m}$ thick epilayer, the following values were obtained:

- (1) $\mu = 5226 \text{ cm}^2/\text{V}\cdot\text{sec}$
- (2) $\rho_{\square} = 83.2 \Omega/\square$
- (3) $\rho = 1.7 \times 10^{-2} \Omega\cdot\text{cm}$
- (4) $N_D - N_A = 6.9 \times 10^{16} \text{ cm}^{-3}$

4.3.2 The "Spin-on" Oxide Approach

For the spin-on oxide, various concentrations of Ga in SiO_2 were tried starting with 10a/o GaO and ending at 95 a/o Ga. No conclusive results were yet obtained and the test is continuing.

Some difficulty (mostly financial) was experienced in obtaining gold, so ruthenium was tried. The work function of this metal is close to that of gold, but the light transmission is higher. Without A-R coating

the solar cells obtained with $.025 \text{ cm}^2$ area, averaged .500 volts open-circuit voltage and .15 mA short-circuit current. It was found that the length of the cycle was extremely temperature dependent. More tests are planned. The major advantage of ruthenium is that it adheres better to the oxide than does gold; the grid contact could therefore be aluminum, thus allowing thermo-compression or ultrasonic bonding to each cell. The procedure for the use of ruthenium is as follows. First, ohmic contact to the back side of the wafer via the Au-Ge evaporation and alloying, as previously described, is done. The Gallium-Silica glass is next applied to the front surface of the wafer and cured. A coat of ruthenium is spun on at 3000 rpm and baked at 300°C for 7 minutes; a second coat is then applied and baked on. The aluminum grid contact is evaporated through a metal mask and the wafer coated with Shipley a-o resist exposed and developed. The wafer is then etched in the Ion Milling machine for 45 seconds and the resist removed with acetone. The cells are now ready for testing.

4.3.3 Electrolytic Etching of Grain Boundaries

A sample of polycrystalline material was divided into three pieces - (a) one was left untreated, (b) one piece was etched in the presence of light with the material at a positive voltage, and (c) one piece was etched in the presence of light with the material at a negative voltage. Only the negatively biased piece showed photovoltaic action with the best cell having an open-circuit voltage of 500 mV and a short-circuit current of .21 mA.

The cell area is $.025 \text{ cm}^2$.

The possible chemical reactions are now being investigated and will be reported later.

4.3.4 Polycrystalline Solar Cells

A wafer of polycrystalline gallium arsenide grown on a polycrystalline n+ substrate was made into the conventional $.025 \text{ cm}^2$ solar cell using the spin-on oxide and the last of our gold for a collector and grid. The cells ran between 580 mV V_{OC} with .2mA I_{SC} and 700 mV V_{OC} with .3 mA I_{SC} .

4.3.5 Stability of MIS Solar Cells

The room in which these tests are to be run is in the process of being air conditioned and work has been temporarily halted. A reliable method of mounting the test cells is also being worked out.

Fig. 19 Photovoltaic characteristics of the best of the cells made by electrolytically etched polycrystalline substrate.

Fig. 20 Grain boundaries in unetched part of eafer (mag = 200x).

Fig. 21 Surface of negatively electrolytically etched grain boundaries — note increase in boundary width (mag = 200x).

Fig. 22 Electrolytically etched grain boundaries (GaAs) with microscope focused on the bottom of the grain boundary (mag = 200x).

5.0 CHARACTERIZATION TECHNIQUES FOR POLYCRYSTAL MATERIALS

During the course of this program, a number of new analytical techniques have been developed specifically to study grain boundaries and polycrystal materials. In addition, a number of measurements commonly used on single crystal materials have been utilized. A brief description of these techniques, and an assessment of their usefulness and sensitivity as applied to grain boundaries and polycrystal materials is provided in the following sections.

5.1 Routine GaAs Layer Characterization

Several methods are used for the routine characterization of GaAs epilayers and polycrystal layers on foreign substrates. These are capacitance-voltage (C-V), Hall, and SEM measurements. Capacitance-voltage characteristics are used on n-type GaAs to measure carrier concentration as a function of distance from the epilayer surface. Hall measurements are used on GaAs grown on non-conducting substrates (usually S.I., GaAs) to obtain carrier concentration and Hall mobility for either n- or p-type material. SEM measurements are used primarily on polycrystal material to observe the surface morphology and apparent grain size, and in the microprobe mode to determine the composition of small areas ($\sim 1\mu\text{m}$).

All these techniques are simple, and therefore suitable for routine characterizations. Schottky diodes for C-V profiling are formed on clean

GaAs surfaces by the vacuum evaporation of Au or other metals. Carrier concentration as a function of depth into the layer is obtained from the variation of diode capacitance with reverse bias. This technique is used universally, and commercial equipment exists which displays $n(x)$ directly. It is necessary to obtain Schottky diodes with fairly low reverse leakage current in order to measure the capacitance; this makes the technique difficult to apply on p-type GaAs or polycrystal material, due to poor MS diode characteristics.

Hall measurements are performed in the van der Pauw configuration on GaAs grown on insulating substrates. Sample preparation can vary in degree of complexity depending on the desired accuracy of the results. Measurements are usually made at room temperature and 77K to obtain a measure of the degree of compensation in the material. These measurements have been discussed widely in the literature. The Hall and C-V measurements are used as simple techniques to keep track of the quality of the GaAs layers being grown. For polycrystal material, these measurements are usually made on single crystal layers grown simultaneously, and provide an upper limit to the material quality.

The SEM is a very simple method to provide a qualitative measure of polycrystal GaAs grain size and growth morphology. The x-ray microprobe attachment allows measurement of the composition of small areas, using a commercial instrument with the attendant ease of operation. Measurements are semi-quantitative ($\pm 3-4\%$ of major constituents and $\pm 100\%$ of minor ($< 2\%$))

constituents) and detection limits are $\sim 0.1\%$. The measurement is, however, very easy and useful for routine characterization and examination of alloying with foreign substrates.

5.2 Electron Beam Induced Current

This measurement technique utilizes the SEM to measure minority carrier diffusion length in either n- or p-type GaAs, and to determine relative collection efficiency in polycrystal GaAs layers.

In the first measurement, the GaAs layer is cleaved or polished perpendicular to the plane of a collection junction (p-n junction or Schottky barrier), and the electron beam is aimed parallel to the plane of the junction, and is scanned along this surface perpendicular to the junction. Carriers excited by the electron beam diffuse to the junction, where they are collected. This collected current is an exponential function of distance between the electron beam excitation and the junction and can be analyzed to yield minority carrier diffusion length. This analysis is complicated by the effects of blooming of the electron beam via primary electron scattering. This effect can be particularly severe for material with short diffusion lengths ($\sim 0.5\mu\text{m}$). These points have been discussed in detail in the literature⁽¹⁾.

This technique can be a rapid method for diffusion length determination if the appropriate instrumentation is available for the SEM, if a standard sample configuration and preparation technique is available, and if the diffusion length is long enough to allow beam blooming effects to be

taken into account simply. These conditions are not met often in polycrystal materials and as a result EBIC measurements of diffusion lengths are not made routinely in polycrystal samples.

In the second measurement, the electron beam is directed onto the sample perpendicular to the collection junction (rather than parallel to the junction). The junction may again be either a (thin) Schottky barrier or a p-n junction. For polycrystal material, the Schottky barrier is used most often. The electron beam is rastered across the sample, and the collected current is used to modulate the intensity of a video monitor, leading to an e-beam induced current picture of the sample. In polycrystal material, areas such as grain boundaries, which have enhanced carrier recombination or built-in fields which reduce carrier collection, appear as dark areas. This technique is a very rapid method of qualitatively determining the effect of grain boundaries on current collection. Resolution is limited by the blooming of the electron beam to about $1\mu\text{m}$. This is a useful measurement to qualitatively observe differences in grain boundaries and grains which sometimes do not appear morphologically.

5.3 Secondary Ion Mass Spectrometry (SIMS)

SIMS is one of the most sensitive methods available for determining chemical composition. It has a typical sensitivity in the sub ppm range; for example, in GaAs state-of-the-art instruments are capable of detecting concentrations of Te and O in concentrations in the 10^{14}cm^{-3} range.

Spatial resolution is moderate ($\sim 100\mu\text{m}$), while depth resolution is very good ($\sim 1\mu\text{m}$). It is therefore an excellent tool for profiling composition of device structures. Concentrations are generally relative, however, unless a calibration can be performed at the same time with a known standard.

Using the Cornell University machine, we have been unable, after numerous attempts, to measure the chemical composition of grain boundaries in polycrystalline GaAs. This is mainly due to the two-dimensional nature of the grain boundary. Although concentrations of impurities segregated at the grain boundary may be quite large, the effective concentration over the probed volume is extremely low due to the narrow width of the grain boundary region. It appears that only by cleaving along the grain boundary in situ, as demonstrated by Kazmerski at the recent Photovoltaics Device and Measurements Conference, can sufficient sensitivity be obtained for investigating segregated species. This appears far easier in Si where in situ cleaving frequently exposes a grain boundary, while in GaAs, only rarely (1%) is a grain boundary exposed. Therefore, we feel at this time that SIMS cannot realistically be used as a routine tool for investigating grain boundary segregation in polycrystal GaAs and likely other polycrystal III-V materials.

On the other hand, SIMS is a powerful tool for profiling species with relatively high bulk concentrations. An important application in the low-cost solar cell program is the study of diffusion from the substrate into the GaAs overlayers that comprise the active part of the cell. The

technique can be of great potential benefit in identifying unwanted species, their concentrations and distributions which might arise from either the substrate or ohmic contacts. SIMS will be used only in this mode in the future.

5.4 Deep Level Transient Spectroscopy

The use of DLTS to investigate grain boundaries in semiconductors, and in particular GaAs, is new and was originated in the work of this program at Cornell. The key to the method involves the use of the depletion region of the grain boundary as the DLTS capacitor; thus, information is provided about deep levels contained only in this volume and not in the surrounding bulk. In this regard, the method differs substantially from the usual method in which the DLTS capacitor is the depletion region of a Schottky barrier evaporated on the surface. Even if the grain boundary extends from the barrier into the bulk, it is generally difficult to separate bulk levels from the grain boundary levels in this case.

The method has high sensitivity and is capable of detecting deep level concentrations 10^4 times smaller than bulk donor concentrations. It is one of the few available methods for studying nonradiative electronic processes in semiconductors, in particular those associated with structural defects. If the deep level is associated with an impurity atom, it is possible to identify the species through its characteristic energy and emission rate. The technique therefore gives chemical information of electrically active species.

This technique has great potential in grain boundary studies and much related fundamental work remains to be done. We believe that it may be possible to resolve the question of whether the properties of grain boundaries in GaAs are intrinsic or extrinsic, a question that has an important bearing on efforts to modify grain boundary properties. The method is versatile in that different levels can be brought into prominence by adjusting the method of excitation. The method has a bright future for the study of grain boundaries, provided its full potential is developed.

5.5 Photo-Induced Transient Spectroscopy

Photo-induced transient spectroscopy (PITS) is a transport technique which detects the transient rise or decay of the sample photocurrent during chopped illumination. A typical PITS spectrum is obtained by sampling either the photo current rise (R-PITS) or decay (D-PITS) at two points in time, with the difference $\Delta I = [I(t_1) - I(t_2)]$ recorded continuously as a function of temperature. Any peaks observed in the spectrum will correspond to a trap emission rate e_t which is directly proportional to the sampling rate $\Delta t^{-1} = (t_2 - t_1)^{-1}$. Successive temperature scans at different sampling rates can therefore determine both the trap energy and capture cross section, assuming a single-exponential rise or decay.

The detection of traps at grain boundaries can be accomplished by the use of ohmic surface contacts in the use of semi-insulating substrate material, or a semi-transparent Schottky barrier over the grain boundary in

the case of conducting substrate material. The use of photo-excitation allows the filling of both electron and hole traps. Current injection can also be used, although its efficiency will be determined by the amount of band bending possible. PITS measurements can be made on samples with very high leakage currents, with transients several orders of magnitude below the equilibrium current being detectable. The degree of trap filling is a function of how much the quasi-Fermi level is moved during illumination, and hence the photo current should be as high as possible. Nevertheless, only electron traps above the equilibrium Fermi level and hole traps below the equilibrium Fermi level will be observable.

The interpretation of PITS data will depend on the degree of trap filling, carrier re-trapping (if any), and potential recombination at deep levels. Traps with activation energies from $\sim 0.10\text{eV}$ to mid-gap can be observed over the temperature range of $60\text{-}500^\circ\text{K}$ with trap emission rates of $50\text{-}1500\text{ sec}^{-1}$. Detectable trap concentrations are on the order of 10^{12}cm^{-3} or above, although this will depend on the number of competing trap levels present.

Equipment required includes a monochromatic light source, high-speed current amplifier, and lock-in or double boxcar detectors. The equipment complexity is somewhat less than for DLTS since no carrier signal demodulation is required. Once the experiment is set up, required monitoring will primarily involve maximizing the signal gain without overloading the amplification chain during the entire temperature scan.

5.6 Scanning Light Microscopy (SLM)

SLM involves the use of a finely focused spot of light (approximately $1\mu\text{m}$ diameter) to excite the specimen. A variety of responses can be measured; examples are reflectance, photoluminescence, short-circuit photocurrent, and open-circuit photovoltage. A map of the spatial variation of the response is obtained by raster-scanning the spot across the specimen by means of electrically-driven scanning mirrors.

Although smaller effective spot diameters can be obtained in a scanning electron microscope operated at low voltage, the advantage of the SLM is its simplicity and the ease with which the system can be integrated into the measurement system (e.g., there are no restrictions imposed by a vacuum chamber). In addition, by using high-quality optics, the field of view can be made very large (covering a whole wafer), as demonstrated by a system developed at the National Bureau of Standards.

Much of our work has emphasized the use of SLM to investigate the electronic structure of grain boundaries in GaAs through measurements of photocurrent and photovoltage. We showed that the internal fields associated with the grain boundary could be viewed directly with this technique, and that it could be used to directly measure the minority carrier diffusion length in the vicinity. We also showed by this means that the band bending at the free surface and at the grain boundary are comparable (barrier height is 0.6-0.8eV). Since the electrical measurements are made across the grain boundary, these can only be performed on epilayers on semi-insulating sub-

strates, or bulk bicrystals, and not on epilayers on conducting substrates. In the latter case, the response tends to be shorted by the substrate.

Because of the difficulty in investigating specimens with conducting substrates, i.e., realistic solar cell structures, by these means, our current work emphasizes techniques which do not have this limitation. An example is spatially resolved photoluminescence. Here, the specimen is excited locally by the SLM and the same optics are used to collect the luminescence from the same small area. This technique promises to yield information about donor segregation at the grain boundary and about recombination processes at the grain boundary.

5.7 Scanning Auger Potential Profiling

The traditional method for determining the majority carrier transport properties in a single crystal semiconductor sample is through the measurement of the dc conductivity. The minority carrier transport properties are deduced from photoconductivity experiments. As a first effort to understand the problems involved in the fabrication of high efficiency polycrystalline solar cells, we have focused our attention on the measurement of the majority and minority carrier transport properties of a sample containing a single grain boundary.

In order to measure the majority carrier transport properties on a microscopic sample, we have developed a new technique based on Auger spectroscopy. A potential is applied across the grain boundary and the

Auger spectrum is measured as a function of location along the sample. The shift of the Auger spectrum can be used as a voltmeter with a voltage resolution of approximately a tenth of a volt and the spatial resolution of a half micron, which is the beam size. A jump in the voltage is observed at grain boundaries which have internal field and are electrically active.

The important parameters which are experimentally determined are the voltage drop across the grain boundary (ΔV) and the width over which the voltage drop occurs (W). The majority carrier transport which determines the potential profile can be understood in terms of space charge limited current:

$$J_{sc} = \frac{\epsilon \mu (\Delta V)^2}{W^3}$$

where ΔV is the voltage drop across the depletion region and W is the depletion width. The space charge limited current through the grain boundary determines the electric field in both the single crystal region and grain boundary, and the experiment measures the actual voltage distribution. Knowledge of the current-voltage relationship for majority carrier transport is key to understanding the high series resistance observed between grains and examination of post-growth treatments which might alter or passivate the grain boundaries.

The SAM profile measurement has proven valuable to understand the majority carrier transport in large grain polycrystal materials. The measurement is, however, rather tedious and time consuming and certainly would not be considered a routine measurement. The spatial resolution of the SAM is $\sim 0.5\text{--}1.0\mu\text{m}$, thus, quantitative measurements are limited to materials with relatively large grains ($>10\mu\text{m}$). Since current polycrystal materials on low cost substrates generally have $\sim 1\mu\text{m}$ grains, the SAM potential profiling has not been utilized. As demonstrated by Kazmerski, the SAM profiling has proven useful in cast polycrystal Si where the grains are larger. We anticipate that the SAM profiling could again become important with development of larger grains and most importantly, in understanding the details of carrier transport around grain boundaries with various treatments to passivate or neutralize their adverse effects.

5.8 Schottky Barrier Dark I-V as a Function of Temperature

This measurement is particularly well suited for determining the effects of grain boundaries on excess junction leakage current. An array of small metal dots are deposited on the GaAs surface to form Schottky barriers. Some of these will lie over the intersection of one or more grain boundaries with the GaAs surface; some will lie in single crystal areas, if the crystallite size is larger than the deposited metal dots. By measuring forward I-V characteristics, the excess current due to grain boundaries can be measured.

It has been found experimentally that all GaAs Schottky diodes could be characterized by the sum of two forward bias current components: one which exhibits "ideal" Schottky behavior (i.e., $I = I_{01} \exp[eV/n_1 kT]$, with $n \cong 1.04$), and one which represents the excess current (i.e., $I = I_{02} \exp[eV/n_2 kT]$, with $n_2 > 2$). The temperature dependence of the two components can be used also to separate the ideal behavior (constant n_1) from the leakage (temperature-dependent n_2). The temperature dependence of the leakage component, and its variation with epilayer doping, can be used to assist in modeling the excess current mechanism and in device design.

This measurement technique is straightforward in its application. The main consideration experimentally is that the Schottky diodes be uniform in their characteristics across a single crystal specimen, so that deviations from ideality can be identified with grain boundary effects. We have assured this by depositing aluminum in situ directly following growth of the GaAs layer in the MBE apparatus. Schottky diodes of nearly as good uniformity can also be produced by vacuum deposition of Au in a standard evaporator, if careful wafer handling procedures are followed. The variable temperature stage used for I-V measurements consists simply of a copper pedestal cooled by cold flowing N_2 gas. Temperature is measured by a commercial resistance thermometer soldered to a Mo plate with In. The sample to be measured is similarly fixed to the Mo plate.

This simple technique has been extremely useful, allowing us to assess the relative leakage of various grain boundaries, and to identify

grain boundaries which show no excess current. This identification permits further extensive investigation and comparison of "good" or passivated or inactive grain boundaries vs. "bad" or active grain boundaries. It is particularly applicable to systems where Schottky barrier solar cells are under consideration. For p-n junction cells, similar measurements using an array of p-n junction mesas should yield useful data.

5.9 Photoresponse

The spectral photoresponse (I_{sc} vs. λ) of a solar cell is important for both routine evaluation and cell to cell comparison as well as thorough analysis to extract quantities such as minority carrier diffusion length. The measurement is also important in understanding and modeling the double layer (AlGaAs/GaAs) Schottky barrier solar cell. Spectral photoresponse is a very easy (3-5 minute) measurement as long as good facilities exist for the measurement. Care in instrumentation and standards are required in order to achieve good accuracy ($<5\%$) in relative photoresponse. Establishing absolute quantum efficiency requires real care and special instrumentation to insure that the entire solar cell is uniformly illuminated with monochromatic light. Fortunately, relative response is usually adequate and all cells are so characterized. The analysis for minority carrier diffusion length is done by computer fit to the photoresponse curve and is usually done of a group of cells with a relatively similar response. The accuracy of the calculated diffusion length is not particularly good ($\pm 25\%$) and usually direct EBIC

or SLM measurements yield better values. These techniques, however, are limited to measurements of diffusion length $>1\mu\text{m}$. At less than $1\mu\text{m}$, these techniques are no longer useful, and a fit to the photoresponse data provides the best information on diffusion length. Because of the extremely short diffusion lengths in current polycrystal GaAs ($\sim 1\mu\text{m}$ grain size), the photoresponse measurement is used to extract an "effective" diffusion length for the small grain material.

6.0 REFERENCES

1. A. M. Sekela, D. L. Feucht and A. G. Milnes, "Diffusion Length Studies in Gallium Arsenide", 5th International Symposium on Gallium Arsenide and Related Compounds, 1974 (Inst. Phys. Conf. Ser. No. 24, Chapter 5)