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DEVELOPMENT OF HIGH EFFICIENCY CASCADE SOLAR CELLS

Quarterly Technical Progress Report No. 3

MASTER

March 31, 1980

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

Research Triangle Institute
Research Triangle Park, North Carolina

U.S. Department of Energy

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QUARTERLY
TECHNICAL PROGRESS REPORT NO. 3

DEVELOPMENT OF HIGH EFFICIENCY CASCADE
SOLAR CELLS

March 31, 1980

Contract XM-9-8136-1 under DOE EG-77-C-01-4042
RTI Project 41U-1846
Solar Energy Research Institute
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Quarterly
Technical Progress Report No. 3
DEVELOPMENT OF HIGH EFFICIENCY CASCADE SOLAR CELLS
Contract XM-9-8136 under DOE EG-77-C-01-4042
March 31, 1980

Introduction

This report summarizes the work conducted under the present contract during the quarterly period 1 January to 31 March 1980.

During the present reporting period, work has concentrated on the following major areas:

AlGaAsSb/GaAsSb Materials Development

GaInP Materials Development via VPE

GaAlAs/GaAs Cell Development

OM/CVD Studies at NSCU

Progress in each of these areas is summarized below.

AlGaAsSb Materials Studies

Fabrication of individual AlGaAsSb wide bandgap and GaAsSb narrow bandgap cell components of the AlGaAsSb/GaAsSb cascade cell has been previously reported, and efforts to improve the electrical properties of these junctions have continued during the past quarter. In addition the remaining component of this cascade materials system, the AlGaAsSb connecting junction, has now been successfully fabricated for the first time.

V-I characteristics for two different AlGaAsSb connecting junctions grown on compositionally graded GaAsSb layers lattice matched to GaAs substrate material are shown in Figure 1. Tunneling behavior is observed in Figure 1a at a bandgap of approximately 1.6 eV (all bandgaps inferred from layer compositions as measured by electron microprobe). As the Al concentration in the solid is increased from $\approx 8\%$ to $\approx 42\%$ and the bandgap approaches ≈ 1.9 eV, the negative resistance region begins to disappear as shown in Figure 1b. This behavior was also observed in AlGaAs tunnel diodes and is attributed to the increased difficulty in achieving high doping levels with increased bandgap. This is the first time that tunneling behavior has been observed in a quaternary alloy.

Vert: 0.02 mA/div Hor: 0.05 V/div

a. $E_g \approx 1.6$ eV

Vert: 0.01 mA/div Hor: 0.05 V/div

b. $E_g \approx 1.9$ eV

Figure 1. V-I characteristics for GaAlAsSb p^+-n^+ diodes of different bandgaps ($A \approx 10^{-2} \text{ cm}^2$).

Figure 2 shows the effect of reduced temperature on the 1.6 eV diode characteristic. At room temperature current peaks occurred between 25 and 35 mA/cm² (not corrected for series resistance) for small area mesas (6.4x10³ cm² to 3.1x10² cm²). Cooling the sample to near 77 K is seen to decrease both the peak current, I_p , and valley current, I_v , and to increase the I_p/I_v ratio from about 0.8 to 3.5, as expected by theory.

In all the tunnel junctions, Te and Ge were used as the n⁺- and p⁺-type dopants, respectively. Good crystalline quality of the quaternary layers was inferred from narrow, well-resolved peaks of the X-ray diffraction patterns.

AlGaAsSb top cells have also been fabricated with bandgaps in the 1.7 to 1.8 eV range. Figure 3 illustrates spectral response data obtained on a top cell. The rapid decrease in spectral response at photon energies above 1.8 eV results from the absence of a window layer in this particular sample and may also be indicative of poor diffusion length material. Subsequent experiments will include evaluation of samples equipped with a window layer.

In growing both AlGaAsSb top cells and tunnel junctions, considerable attention has been directed toward obtaining reproducible layers with controlled Al content. The electron microprobe is being used to measure the atomic percent of aluminum in the quaternary layers; these data are being correlated with the percent Al employed in the melt to develop solidus data for the quaternary. The results of Al concentration measurements made on several samples are shown in Table 1.

While the bulk of the research effort this quarter has been with the tunnel junction and the top cell, there have been important findings with the GaAsSb bottom cell. The problem of low open circuit voltage, V_{oc} , has remained. V_{oc} values are generally 0.4 to 0.6 V for diodes with bandgaps from 1.2 eV to 1.3 eV. Speculation continues that this is caused by either surface effects, crystalline defects, or chemical impurities. It was also speculated that using magnesium diffusion to produce the top p-layer, as opposed to growing a germanium-doped layer, might improve V_{oc} . The results of growth experiments were as follows: after etching the edges of the substrate, the entire growth area (approx. 80% of 1 cm x 1 cm) showed a diode characteristic with $V_{oc} \approx 0.35$ V; while this voltage isn't impressive, this is not the first time such large area diodes have been grown. When small mesas were etched, V_{oc} increased to ≈ 0.45 V with current densities about 1 mA/cm² to 4 mA/cm². Another interesting feature of these diodes was the breakdown voltages in the 8 to 10 V range.

Vert: 0.2 mA/div

Hor: 0.1 V/div

Figure 2. Effect of temperature on V-I Characteristics of GaAlAsSb n^+-p^+ diodes (upper curve: 300 K, lower curve: ≈ 77 K).

Figure 3. Spectral response of AlGaAsSb top cell ($E_g \approx 1.8$ eV, no window layer or AR coating).

Table 1. Electron Microprobe Results Indicating Aluminum Content of AlGaAsSb Alloys.

Run No.	Structure	Al in Melt [mg/g(Ga)]	Al in Solid (At.%)
116	Tunnel Junction	10.3	32
117	Top Cell	13.5	41
118	Tunnel Junction	15.0	42
119	Top Cell	3.1	26
120	Top Cell	2.1	18
121	Tunnel Junction	2.1	15
122	Tunnel Junction	1.8	8
123	Top Cell	2.1	21
124	Tunnel Junction	2.1	13

Note: All Al containing melts had Sb/Ga ratio of 1.0; melts saturated with GaAs source crystals. Growth carried out on GaAs_{0.9}Sb_{0.1} layer ($\approx 5.7\text{\AA}$ lattice parameter).

Recent acquisition of an EBIC attachment for the scanning electron microscope has resulted in additional diffusion length data on cleaved p-n junctions. An EBIC scan obtained on a GaAsSb junction is shown in Figure 4. Diffusion lengths estimated from the trace were ($L_n \approx 0.7 \mu\text{m}$ and $L_p \approx 1.1 \mu\text{m}$; these values compare favorably with a $1.8 \mu\text{m}$ collection depth measurement obtained by the gamma cell technique.

Finally, a tunnel junction has been grown on a 1.3 eV bandgap bottom cell for the first time. As shown in Figure 5, this structure was characterized by a V_{oc} of 0.6 V and a current density of approximately 3 mA/cm^2 . This current density is low but should improve upon reducing the p-layer thickness. These values are comparable to bottom cells without the tunnel junction. The spectral response for this structure is shown in Figure 6. The tunnel junction appears to aid in current collection slightly and does not appear to have deleterious effects on the bottom cell.

GaInP Materials Studies

VPE GaInP work has thus far demonstrated the ability to (1) grow mirror-like layers and (2) produce stepwise changes in composition of 3.3% InP per step via the introduction of step-wise changes in the HCl flow rates over the Ga and In sources without interrupting the growth process. This confirms that the system is achieving the response times ($\approx 5 \text{ sec}$) for which it was designed; layers were obtained at a growth temperature of 600°C and total flow rates on the order of 600 sccm. Growth rates were approximately 2 to $3 \mu\text{m/hr}$.

Refinements in the Ga and In source boat design are currently being incorporated to effect a more complete conversion of HCl to the Ga and In monochlorides. At this time, each source (Ga and In) uses two vertical boats with the top boat converting approximately 70% of the incident HCl to the respective monochloride. The bottom boat only converts approximately 3% of the remaining HCl. The reduced efficiency of the bottom boat is due to the gases flowing by this boat without interacting with the melt surface. This problem is being remedied with a new boat design which keeps the supplemental H_2 flow (for each source) separated from the HCl mixture and allows the unreacted HCl to impinge directly on the surface of the melt in the second (and/or third) source boat. This will ensure that each source boat operates at approximately 70% conversion efficiency as does the top or primary boat. A three-stage source will thus be

Figure 4. SEM/EBIC scan across GaAsSb p-n junction (3200X).

Vert: 0.05 mA/div

Hor: 0.2 V/div

Figure 5. V-I characteristic for AlGaAsSb connecting diode grown on GaAsSb bottom cell. ($V_{oc} \approx 0.6$ V, $J_{sc} \approx 3$ mA/cm²)

Figure 6. Spectral response of AlGaAsSb tunnel junction/GaAsSb bottom cell combination.

expected to give an overall conversion efficiency of 97% which is nearly equal to the maximum theoretical conversion efficiency.

P-type doping has been attempted using a DMCd/H_2 mixture but to date has not resulted in p-n junctions. At this time, it is not clear whether the DMCd has decomposed in the gas cylinder or whether the Cd is not being incorporated into the grown layer or is simply not being electrically activated in the layer. Matheson Gas Products, the supplier of the dopant gas mixture, has discontinued a similar dopant gas mixture (DMZn in H_2) because of stability problems. Since these gaseous dopant sources are no longer available, an alternate means of introducing p-type dopants is being incorporated into the system. It will use the liquid organometallic DMCd as a constant vapor pressure source and a small capillary to provide diffusion limited dopant flow in the .01 sccm (or less) range.

A suitable p-dopant for the tunnel junction required with the cascade cell must satisfy both the high doping level requirement ($\approx 10^{19}/\text{cm}^3$) and an abrupt doping profile. Zn has already been demonstrated to satisfy the high doping levels required ($\approx 10^{19}$ holes/ cm^3 reported for $\text{In}_{.49}\text{Ga}_{.51}\text{P}$) [Ref. 1]. Also reported was a factor of 3 higher p-doping levels obtained in this InGaP compared with that obtained in GaAs using similar growth conditions. Unfortunately, Zn tends to be a relatively fast diffusing specie, especially at the customary growth times and temperatures (600 to 800°C), and is therefore unsuitable as the p-type dopant for the tunnel junction.

Amphoteric dopants such as Si or Ge represent potentially convenient alternatives insofar as gaseous sources being readily available; however, these tend to show a preference toward n-type behavior and, by their nature, tend also to be self-compensating so that lower mobilities generally are obtained. Thus, Si and Ge do not appear to be attractive and will not be pursued.

Ion implantation is an alternative doping approach for p⁺-type doping that can provide a much broader range of p-type dopants. Dopants such as Be , Mn and Mg in addition to Zn and Cd can easily be investigated using this approach. High doping levels have been achieved with Cd in GaAs using ion implantation [Ref. 2,3]. Hole concentrations in excess of $2 \times 10^{19}/\text{cm}^3$ were reported for both ion implanted Cd and Zn ; this level is adequate for the tunnel junction. This paper also notes that the in-diffusion of Zn or Cd is typically less than for the same impurity

diffused in from a vapor source; thus, subsequent layer growth would be less apt to interfere with the p^+ doping profile.

Heavily doped n-layers still remain somewhat of a question. Doping levels of at least $2 \times 10^{18}/\text{cm}^3$ have been reported using Se (from H_2Se) in $\text{In}_{.49}\text{Ga}_{.51}\text{P}$ [Ref. 1]; somewhat higher doping levels should be possible and will be investigated further. Sulfur will also be considered as an n^+ dopant.

Planned effort includes retrofitting the growth system with the new source boats, installing the new dopant source, and continuing growth of GaInP.

AlGaAs/GaAs Cell

Work has continued in the AlGaAs/GaAs cascade cell, primarily under AF Contract F-33615-78-C-2077.

Three different cascade cell configurations have been considered; these are shown in Fig. 7. The principal difficulty with the 7-layer structure (a) that utilizes the Ge-doped top cell is low open circuit voltage (1.5 to 1.6 V).

Cells fabricated using Be doping for the top cell (b) also give low open circuit voltages (1.6 to 2.0 V) and, in addition, are quite irreproducible. In some samples the top cell is completely shorted. (We believe this results from excessive Be diffusion through local imperfections produced by the underlying highly doped Te layers). The growth of a thick n-AlGaAs layer using melts that are saturated at successively lower temperatures results in some improvement in yield, i.e., more devices having two active junctions. However, work along this line is still in progress.

To take advantage of the more favorable properties of the p^+ on n^+ tunnel junction at high bandgaps, a cascade cell with 1.9 eV AlGaAs was fabricated on a p-type substrate (such that both bottom and top cells are n on p rather than p on n). Ge and Sn were used as the dopants for the cells, while Te was used as the dopant for the n^+ window layer. In this device V_{oc} was in the 1.5 to 1.8 V range and the short circuit current was low. Further studies of this structure will be conducted as time permits.

Experimental efforts in the immediate future will focus on growth of structure (b) and also on structure (a) after the Ge-doped top cell has been improved. Structure (c) will be studied when problems relating to Be diffusion have been resolved.

Fig. 7. Cascade Solar Cell Configurations

OM-CVD Studies at NCSU

The major new result at NCSU during the past quarter has been the successful growth of semiconductors using the new OM-CVD system. Several good growth runs have been completed for the growth of GaAs layers. Typical growth rates appear to be in the range of 0.1-0.2 μm per min, which is about the expected growth rates. The layers as grown appear to be n-type with Schottky barrier breakdown voltages using a Hg probe of 15-20 volts. This would imply doping densities in the range of 5×10^{16} to $1 \times 10^{17}/\text{cm}^3$. However, this needs to be verified by Hall measurements and Hall samples are presently being grown on semi-insulating GaAs substrates.

Several AlGaAs growth runs have been made and the resulting layers have been shiny with good surface morphology. Sample compositions up to 60% AlAs have been obtained.

Plans at NCSU during the next period are to move ahead with the OM-CVD work. Studies are underway to investigate the optimum flow rates for the As/Ga ratio to achieve the highest quality layers. At the same time studies of AlGaAs layers will begin.

Other Activities

Efforts are currently underway to provide GaAs and GaAlAs single junction solar cells with two layer antireflection coatings and to mount these devices in packages convenient for handling and evaluation. This packaging technique will be used later with cascade solar cell structures.

A liquid filter has been obtained for use with the solar simulator which is being recalibrated using a standard cell obtained from NASA/LRC.

A Miller capacitance profiler has been ordered and will be available in the near future to more accurately evaluate device carrier concentration profiles.

Work is also proceeding at NCSU on the design of an ohmic contact geometry for the cascade cell for concentrator applications.

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