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EMERGING MATERIALS FOR SOLAR CELL APPLICATIONS—
ELECTRODEPOSITED CdTe

Third Quarter Report for Period September 1—November 30, 1979

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Solar Energy

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EMERGING MATERIALS FOR SOLAR CELL APPLICATIONS — ELECTRODEPOSITED CdTe

THIRD QUARTER REPORT
FOR PERIOD SEPTEMBER 1— NOVEMBER 30, 1979

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DECEMBER 20, 1979

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ABSTRACT

Major emphasis during the period was centered on improving the material properties of electrodeposited CdTe. Using newly devised means for peeling thin CdTe films off the ITO-coated glass substrates, it was possible to accurately measure material density and electrical resistivity. Density proved to be 40% below the bulk CdTe figure of about 6 gm/cm^3 , while resistivity of supposedly doped CdTe films exceeded $10^5 \Omega - \text{cm}$.

These findings prompted initiation of a beneficial change in plating procedures which increased the thin film polycrystalline CdTe density to the bulk value while, at the same time, good columnar growth was obtained. Films made under the old plating process were made into Schottky diodes showing good uniformity and V_{OC} values generally exceeding 0.5V. Short circuit current of the best of these was 9.5 mA/cm^2 despite the fact that light entered through a thick gold film and was strongly attenuated.

During the forthcoming period a large number of films plated under the new conditions will have been evaluated to see how the columnar growth and greater density affects the performance of photovoltaic devices.

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1. INTRODUCTION

The third quarter of our effort was devoted to improving material properties of electrodeposited CdTe films. Crystallinity of the films was largely improved as columnar grains have been grown. In many cases, the crystallites consisted of one grain from the bottom to the top of the film.

The direct measurement of material resistivity of very thin films on an electrically conductive substrate is a major undertaking. Both Monosolar and UCLA have set forth to develop techniques for separating the CdTe films from the substrate without affecting the material properties. Very encouraging results have been obtained so far on large area 1 μ m thick separated films. The long sought for technique for measuring Hall mobilities in very thin films grown on a conductive substrate seems to be close to realization.

Properties of ITO films produced at UCLA have been studied for optimalization. The best films were produced at a high substrate temperature. The high temperature requirement is so far not compatible with thin film CdTe for making ITO/CdTe heterojunctions. CdTe films were electrodeposited on UCLA produced ITO/glass substrates. No special difficulties were encountered.

2. CdTe MATERIAL CHARACTERIZATION

2.1 Structural Characterization (Monosolar)

Grain structure and morphology of the CdTe films was studied at Monosolar using a high power Nomarski Differential Interference Contrast microscope.

CdTe films electrodeposited on ITO/glass substrates displayed a very smooth and uniform coating up to a thickness of $1\mu\text{M}$ with grain size about equal to the surface roughness of the ITO, ($\pm 0.5\mu\text{M}$). Deposition conditions are similar to those reported in the first and second quarterly reports ⁽¹⁾ . As deposition proceeds, certain grains serve as nucleation centers for larger grains to be developed on the surface. The size of those grains is limited only by the duration of deposition. Figures 1-a,b,c show the gradual development of large grains and the extent of surface coverage on top of an approximate $1.5\mu\text{M}$ thick film of CdTe.

A slide of CdTe/ITO/glass was fractured and a side view of the CdTe film is shown in Figure 2. The individual grains in the uniform CdTe film are seen to grow randomly on top of each other with continuous renucleation of new grains. From the weight of the sample before and after CdTe deposition and from the thickness of the CdTe film as measured on the photomicrograph, a density of $3.6 \pm 0.4 \text{ gm/cm}^3$ is obtained for the electrodeposited CdTe. This density is by far lower than 5.86 gm/cm^3 of bulk CdTe.

This reduced density with many voids between the grains is considered the major cause for the apparent high electrical resistivity of the CdTe material as reported earlier ⁽¹⁾ .

To solve the problem of low density of the CdTe, a considerable effort was spent in reformulating the electrolytes in which electrodeposition takes place. Preliminary results obtained by reducing the pH to 1.5 suggest that the density of the CdTe can be increased. Figure 3a is a side view of a CdTe film deposited under the new conditions.

Fig. 1: Nucleation and growth of CdTe crystallites

1a: Some grains serve as nucleation centers to start large grain growth. The area between grains is uniform CdTe, 0.5μ thick with grain size of about 0.5μ .

1b: As deposition proceeds, new grains are nucleated and old grains grow larger.

1c: The surface is completely covered with large grains some as large as 3μ .

Fig. 2: A side view of a fractured CdTe polycrystalline film.

Fig 3a: A side view of a fractured CdTe film showing columnar growth of grains.

Fig. 3b: Top view of the CdTe film of Fig. 3a.

The density of this film is $6.0 \pm 0.4 \text{ gm/cm}^3$ which is in agreement with the bulk CdTe density. An added benefit of the new deposition conditions as seen in Figure 3a is the growth of continuous grains throughout the thickness of the film. This columnar structure is the most desirable form of thin film polycrystalline material. If carriers generated in the polycrystalline film do not have to cross grain boundaries prior to collection, a considerable source of carrier recombination will be eliminated.

A top view of the sample of Figure 3a is shown in Figure 3b. Refinement of the columnar growth and increase of the lateral dimensions of the columnar grains will be a major subject of future work. The use of single crystal or polycrystalline substrates is expected to lead to epitaxial growth of the thin film semiconductor material at low temperatures using electrodeposition.

2.2 Electrical Characterization (UCLA)

CdTe films were peeled off the ITO substrate by immersion in HCl for several hours. It was determined that a Te-rich conductive layer forms on the surface, yielding erroneous readings for the film sheet resistivity. Another method of peeling the CdTe off the ITO/glass substrate involved etching in HF. Glass was etched in HF in an ultrasonic cleaner for about 30 minutes. One problem with this technique was that the etching was not very uniform and some parts of the film were exposed to HF more than others thus giving rise to conductive (Te-rich) islands on the film. The parts of the film which were not exposed to HF for long times were high resistivity ($\geq 10^5 \Omega\text{-cm}$) and photosensitive.

To avoid the formation of a Te-rich layer, mechanical stripping was employed. "Torr-Seal" epoxy was used to strip films off the ITO and glass substrates. Most of the films obtained had smooth, crack-free surfaces. Contacts were made by etching with bromine methanol followed by indium soldering. Two and four terminal resistivity measurements show resistivities of the order of $10^5 \Omega\text{-cm}$ for all the films that are electrodeposited with indium or gold doped electrolytes.

Resistivity and photoconductivity experiments on electrodeposited CdTe films were for the first time carried out in the plane of the film. The film used was electrodeposited and gold doped. Resistivity was $5 \times 10^5 \Omega\text{-cm}$. Strong dependence of the resistivity on the temperature is indicative of the deep level(s) in the material which are electrically active. Figure 4 shows the variation of dark conductivity with temperature. The slope of the curve gives an energy of 0.4 eV. Type of the material could not be determined by simple dc Hall measurement due its high resistivity. If it is p-type and a close compensation model is used, the ionization energy of 0.4 eV is in perfect agreement with the ionization energy of the gold acceptors. Work is in progress to carry out ac Hall measurements to obtain the mobility values for such films.

A rectangular piece of the same film (2mm x 6mm x 1.2 μM) was used for photoconductivity measurements. Bandpass filters were used for wavelengths .45 μM $<\lambda < 1.1\mu\text{M}$.

The photoresponse curve for $V = 50 \text{ V}$ is given in Figure 5. The relatively broad peak is in agreement with the findings of De Vore ⁽²⁾ who showed that such behavior is expected for very thin films. The drop at low wavelengths is due to surface recombination effects. Photoconductivity at high wavelengths can be explained by the presence of energy levels in the forbidden gap.

Fig. 4: Temperature dependence of dark CdTe conductivity

Fig. 5: Spectral response of CdTe photoconductivity at T=300°K

Dependence of the photocurrent on the intensity of light is shown in Figure 6 with a wavelength of $\lambda=0.7\mu\text{M}$ and an applied voltage of 20V. It is observed that the current varies as the square root of the illumination intensity at room temperature. Such a dependence can be observed if the density of photoexcited electrons trapped above the electron Fermi level is greater than the density of photoexcited electron trapped below the Fermi level⁽³⁾ or if the material is trap free. That our material is not free of traps can be observed from Figure 7 which shows the decay curve of the photoconductivity. This is not a simple exponential decay. It is a complex function of time. The longest time constant is in the order of 4 minutes. Further experiments with samples prepared under different conditions are necessary to be able to get a clear picture of the electronic processes in these films.

Results of the work on Au/undoped CdTe/Ni devices were reported before.⁽¹⁾ Presence of electron traps in these films was shown using the space charge limited currents observed for such devices. This time CdTe films electrodeposited in indium doped electrolytes were used to study the characteristics of Au/CdTe/ITO devices. Figure 8 shows the I-V characteristics of a typical device which is prepared at high deposition potential. An exponential rise of the current is followed by a linear portion corresponding to a high resistance. The exponential part of the curve can be fitted with $I = A \exp\left(\frac{qV}{nKT}\right)$, n changing from 1.1 to 1.75 indicating the effect of recombination in the depletion region. Assuming that the linear part at higher voltages is due to the series resistance and that the effect of the ITO/CdTe contact resistance is negligible, we determined the resistivity values for the material prepared at different potentials.

Fig. 6: Photocurrent vs. light intensity at $\lambda=0.7\mu$

Fig. 7: Time decay of photoconductivity

Fig. 8: Dark I-V characteristics of a Au/CdTe device

Fig. 9: Resistivity variation of CdTe material vs. CdTe-electrolyte potential.

Figure 9 shows the results of these measurements. 10 devices were tested at each potential and the distribution of values obtained is shown as bars.

Results are in accordance with the resistivity measurements made on mechanically stripped films, i.e. the electroplated CdTe films are high resistivity with $\rho \geq 10^5 \Omega\text{-cm}$.

3. CHARACTERIZATION OF ITO FILMS (Produced at UCLA)

In continuation of the efforts to develop the $\text{In}_2\text{O}_3\text{:Sn}$ prepared by the activated reactive evaporation techniques developed at the UCLA Materials Department, some studies on electrical characterization of these films have been completed. Results are summarized in the following:

The Sheet resistance as a function of Sn concentration in the In-Sn alloy is shown in Figure 10. It is seen that the sheet resistance decreases rapidly with increasing Sn concentration. Also given in the figure is the integrated (over .4 - 1.2 μM) value of transmittance for these films. It should be noted that, whereas the sheet resistance is a strong function of Sn concentration, the transmittance is only weakly dependent on it.

Electrical resistivity measurements have also been carried out on $\text{In}_2\text{O}_3\text{:Sn}$ (18%) films deposited at temperatures ranging from room temperature to 400°C. The electrical resistivity is found to be strongly dependent on the deposition temperature as shown in Figure 11. The resistivity decreases with increasing deposition temperature. Beyond 250°C the electrical resistivity decreases very rapidly. Transmittance measurements on these films show that films deposited at all temperatures are highly transparent (>90%) over a wavelength region of 0.6 to 1.2 μM .

Fig. 10: Sheet resistivity and transmission vs. Sn concentration of ITO films

Fig. 11: Resistivity vs. substrate temperature of ITO films

4. PHOTOVOLTAIC CELLS

4.1. ITO on CdTe Heterojunctions

ITO films were deposited on p-type CdTe films at UCLA using the newly developed activated reactive evaporation technique. ITO films were deposited at substrate temperatures in the range of 50°C - 400°C. Above 200°C, the CdTe films deteriorated and no useful information was obtained. Below 200°C, good deposits were obtained; however, no diode behavior was observed. The ITO/CdTe contact was rather ohmic. Possible difficulties encountered with this structure are as follows:

- a. ITO resistivity of films deposited below 200°C is several orders of magnitude higher than that of the best ITO deposited 370°C.
- b. CdTe resistivity is several orders of magnitude higher than the optimum desired value.
- c. CdTe surface modifications at high temperatures in the presence of oxygen gas.

4.2 Au/CdTe Schottky barriers

The photovoltaic response of the Au/CdTe Schottky barrier device was improved since the writing of the last report. Both the voltage and the current went up, present values being $V_{OC} = 0.53V$, $J_{SC} = 9.5mA/cm^2$ (quartz halogen lamp normalized to 100mW/cm²). The fill factor is still low at 0.33, which reflects the high material resistivity leading to high series resistance. Figure 12 shows the dependence of J_{SC} on V_{OC} over a light intensity range of 0.002-15 suns. The cell was cooled with forced air and at the high intensity points the light source was turned on for a few seconds only to minimize temperature variations.

Fig. 12: J_{sc} vs. V_{oc} of an Au/CdTe/ITO photovoltaic cell at different illumination levels

The temperature of the cell was maintained at 28-30°C throughout the measurement.

From the relationship $V_{oc} = \frac{AkT}{q} \ln \left(\frac{J_{sc}}{J_o} + 1 \right)$ the diode factor A is 1.1 and the saturation current is 1.2×10^{-10} A/cm².

5. WORK PROPOSED DURING NEXT QUARTER

1. Develop deposition conditions to yield columnar growth of grains.
2. Measure doping levels in CdTe vs. dopant Concentration in electrolytes.
3. Measure carrier transport properties in CdTe.
4. Optimize photovoltaic properties.

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