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EMERGING MATERIALS FOR SOLAR CELL APPLICATIONS—
ELECTRODEPOSITED CdTe

First Quarter Report, February 15—May 15, 1980

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Monosolar, Inc.
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Solar Energy

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EMERGING MATERIALS FOR SOLAR CELL
APPLICATIONS -- ELECTRODEPOSITED CdTe

FIRST QUARTER REPORT
FOR PERIOD FEBRUARY 15 -- MAY 15, 1980

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JUNE 30, 1980

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ABSTRACT

The present program is a continuation of earlier efforts to develop electrochemically deposited films of compound semiconductors and solar cells made from them. Primary objectives include the development and characterization of controllably doped n and p type CdTe films with densities of 5.8 gm/cm^3 , appropriate grain sizes, good film morphology and freedom from pinholes, and carrier concentrations from 10^{16} to $10^{18}/\text{cm}^3$. The end result of the effort is to demonstrate by the seventh month, or September 15, 1980, solar cells over 1 cm^2 in area showing total area conversion efficiencies exceeding 4%.

By the end of the first quarter, milestones were met calling for us to supply characterized n type CdTe films that were reproducible and free from pinholes. Also, prototype electrodeposited CdTe solar cells were fabricated and evaluated. Characterizations of p-type CdTe and ZnTe films were complicated by interferences existing between them and adjacent substrates.

A number of devices, including the glass/ITO/n-CdTe:In/Au Schottky structure and an ITO/n-CdTe:In/p-Cu_{2-x}Te heterojunction, have been fabricated. The highest internal efficiency of the Schottky devices, which have yet to have fingered grids and anti-reflection coatings applied, is 4%. The heterojunction is a larger area device 2 cm^2 in area. It shows promise of meeting the 4% total area efficiency as does the Schottky when grids and A/R coatings are applied.

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1. GENERAL REVIEW

Earlier work at Monosolar under DOE support demonstrated the feasibility of electrodeposited CdTe solar cells but could not address questions of film and device reproducibility. A more complete understanding of the electrochemical variables governing film growth and device performance did not come about until three months ago when Monosolar purchased a Perkin Elmer Atomic Absorption Spectrophotometer for exclusive use in this program. The AA unit has since delineated the concentrations of Cd, Te, and In in electrolytes used to plate films and in films dissolved in acid made at varying plating current densities. These studies, which correlate plating parameters with device performance, were conducted for the original CdSO_4 - type electrolyte and another using a bromide-based system. For both electrolytes, the baths were held at pH values around 1.5 to 2 and at constant temperatures of between 90 and 95° C.

After two months of this work, it was possible to eliminate use of the alternative bromide electrolyte that previously had been used to make cells with higher J_{sc} values than had been obtained in CdSO_4 . Good films of equal short circuit current capability and good V_{oc} are made now in the CdSO_4 electrolyte providing the Te concentration in the electrolyte is held at or close to an optimal value for the exact pH value selected.

Both electrolytes were employed in film plating experiments under alternative constant deposition current and voltage conditions. It will be recalled that the relationship between these plating parameters is determined by

$$V_{dep} = (E_{Cd})_{CdTe} + \Delta V = E_{rest} + \Delta V$$

with $V = n + iR$

where n = overpotential

i = current and

R = film resistance

The rest potential for a particular plating bath pH determines the stoichiometry of the electrodeposited film. Less negative values vs SCE produce an excess of Te, while more negative values increase the concentration of Cd and create n-type CdTe.

Ideally one would wish to plate any substance under constant current conditions to assure uniformity of the deposit, particularly during the very first moments when film resistance is closest to zero and excessively high plating current causes hydrogen evolution and "burning". However, it is not desirable to do this while plating a compound semiconductor whose stoichiometry is a function of the rest and deposition potentials. Experiments verified the fact that to best maintain the film stoichiometry at a desired ratio, the rest potential should be held as close to constant as possible and the current be permitted to vary.

Current plating procedures have been standardized around the constant rest potential approach with additional precautions being taken to eliminate excessive current surges at zero time. Account also is taken of the fact that the desired Te concentration in the electrolyte also is a function of current density.

Adding to the number of variables that must be controlled in order to make good devices are several parameters governing evaporative deposition of gold to form CdTe/Au Schottky diodes and solar cells. Until recently when Monosolar took delivery of a Veeco Model 300 Evaporation system provided by SERI as Government Furnished Equipment, gold films were applied to Monosolar-made CdTe films by our subcontractor, UCLA. Having an in-house capability to apply the gold within minutes after plating a CdTe film to evaluate

the resulting devices immediately thereafter has uncovered the following information of considerable value to present and future work:

- Device efficiency, particularly as governed by fill factor and short circuit current, is, of course, a function of the Au thickness. Optimum results in our case are achieved at transmission values over the visible spectrum of 15% or less. Thinner gold films display excessively high sheet resistance; thicker ones admit no light.
- A bromine methanol etch of the CdTe film prior to Au deposition is beneficial in optimizing factors controlling cell efficiency.
- Porosity of thin gold films used to make Schottky cells allows permeation of air causing junction deterioration. This will necessitate use of a protective window in finalized back window devices. This deterioration fortunately is not caused by a breakdown in the quality of the good ohmic contact now uniformly present between the ITO and the n-CdTe, a reassuring finding indeed. This has been verified by re-etching half of a film that was not coated with Au initially and then applying gold to the second half. The resulting Schottky was again identical to and equal in efficiency to that deposited initially on the first half.

The increased knowledge of quantitative chemical analyses of both the electrolyte(s) and n-CdTe films in particular plus an ability to better control the properties of Schottky devices made possible a decision in late May to freeze plating bath composition and operating parameters and concentrate thereafter on making large area solar cells. There remain certain unknowns in the plating system that are presently the subject of intensive current concern.

However, their effect on cell efficiency no longer is of major concern. It has been found, for example, that both tin and indium in indium tin oxide films, slowly leach out into the electrolyte. Measurements of these sources of contamination are now underway preparatory to undertaking steps for controlling them.

In Monosolar's parallel work electroplating gallium arsenide films on ITO under a company supported program, the same tin and indium contamination plus iron were found independently in EDAX studies at UCLA. The iron was traced back to stainless steel clamps used at Monosolar to hold the substrates (cathodes) during electroplating. These clamps have since been silver plated or covered with photoresist to prevent their leaching out iron and chromium in an environment of hot acidic vapors. It is expected that these steps will result shortly in better device behavior.

2. FILM CHARACTERIZATIONS

In accordance with the program plan, work during the past three month period was concentrated around development of n and p-CdTe films. Simultaneously Monosolar undertook studies leading to the plating of ZnTe films which intrinsically are p type. It had been planned initially that either p-CdTe or ZnTe films could soon be used to fabricate homo- and heterojunction type solar cells respectively over n-CdTe electrodeposited on ITO. It has been found, however, that such cells most likely can be made now by far simpler techniques involving deposition metals like Cu, on the n-CdTe films and converting these metals as the case may be to their tellurides by heat treatment or possibly laser irradiation.

The advantages of the metal deposition approach over use of p-type compound semiconductors are several in number. For one thing, electro-deposition of a second compound semiconductor on top of the first appears very difficult and time consuming to achieve in certain cases. For ZnTe, as an example, an exchange reaction takes place in the electrolyte wherein Zn substitutes for Cd in the original film thus destroying it. Also, deposition conditions vary between n and p types as mentioned earlier, and control is not easily obtainable for a second film being plated atop the first. It thus appears that major attention is best given in coming months to making solar cells by depositing a metal by evaporation or plating or chemical exchange on top of our well-developed n-CdTe films and converting it to the telluride in situ.

In addition to the difficulties enumerated in plating p type compound semiconductor films, we have encountered numerous problems in their characterizations. So far the most suitable plating substrate has been n-ITO. Making measurements of micron-thick p type layers in close proximity to a substrate of opposite type is next to impossible without undertaking work beyond the scope of the current effort. It was decided, therefore, to downplay the importance of p-CdTe and ZnTe films entirely and concentrate instead on the method of making tellurides by depositing the appropriate metal. Characterizations then of necessity will be of the complete devices themselves and not of the thin p layer only.

With these points in mind, the importance of Monosolar's basic n-CdTe layer increases. Here we have assembled a considerable body of knowledge which is new and unavailable elsewhere. Characterizations of these films which were conducted during the past three months will now be reported upon.

a) Optical Absorption Coefficients

Optical absorption coefficients of electrodeposited CdTe films were measured as a function of wavelength. Thin CdTe films were deposited on ITO substrates and reflection and transmission data were obtained for $0.55 \mu\text{m} \leq \lambda \leq 0.78/\mu\text{m}$. This is the region of the solar spectra which is important for our thin film cells.

The absorption coefficients are calculated using the equation:

$$e^{-\alpha t} = \frac{I_t}{I_o} \cdot \frac{1}{(1-R)^2} \quad (1)$$

where

α is the absorption coefficient

t is the thickness of the film and

R is the reflection coefficient

I_t and I_o are the transmitted and incident light intensities, respectively. The above equation is valid for

$$R^2 e^{-2\alpha t} \ll 1$$

and this condition is satisfied for the wavelength region we are working at.

The thicknesses of the films were measured using the infrared interference patterns, and the density of the films was calculated using the thickness value and the measured weight of the film. A value close to 6 gm/cm^3 is obtained. This indicates that there is not porosity in the measured films.

Figure 1 shows the absorption coefficients calculated from Equation (1) for a film of $0.85 \mu\text{m}$ thickness. Previously reported curves a, b, and c also are included for comparison. Curve a is for single crystal CdTe². Curves b³ and c⁴ are for vacuum evaporated polycrystalline films of high resistivity. It is observed that the absorption coefficients of electrodeposited CdTe films are higher than the values reported for single crystal material. Similar behavior was previously reported by Mitchell for his CdTe layers⁵. Ours is an important finding in the sense that electrodeposited CdTe films of less than $1 \mu\text{m}$ thickness absorb 80% of the incident solar spectrum energy. The positive ramifications on reducing the costs for critical material is clear.

b) Resistivity

The resistivities of electrodeposited n-CdTe films were measured by stripping them from their conductive substrates. The removal methods and contacting procedures for the stripped films were previously described⁶. The lowest resistivities measured were in the order of $5 \times 10^4 - 10^5 \Omega\text{-cm}$. Mobility measurements were complicated as described before⁶. Taking the electron mobility values ($\sim 20 \text{ cm}^2/\text{V-sec}$) that we could measure on a few samples, we calculated a carrier density of about $10^{13}/\text{cm}^3$ for the lowest resistivity films available. Although we could not attain lower resistivities, this factor does not seem to be the most important one for our cells. The optical absorption coefficient measurements showed that films which are less than $1 \mu\text{m}$ thick can feasibly be used for our devices. Assuming a film thickness of $0.8 \mu\text{m}$ and a depletion width of $0.3 \mu\text{m}$ ⁶, the series resistance of the unswept region is in the order of 2.5Ω for a 1 cm^2 device.

For a current density of 10 mA/cm² (which is common for CdTe cells) this corresponds to a 25 mV voltage drop across the series resistance. This indicates that it will be feasible to produce efficient cells on our material when resistivity is in the order of 10⁴ Ω-cm.

c) Diffusion Length

Diffusion length is an important parameter for solar cell performance. There are various techniques to measure diffusion lengths in semiconductors. Some of these techniques utilize V_{oc} or I_{sc} measurements and others use a light spot or an electron beam to scan the junction region. Obviously the use of a scanning beam was not possible for our thin film devices. Spectral response measurements are made by shining light from the transparent ITO contact. The results are compared with theoretical curves to obtain the minority carrier diffusion length. Discussion of this method is presented below:

When the light enters from the back ohmic contact, the diffusion component of the photogenerated current can be written in the form of:

$$J_p = \left[\frac{qF_o(1-R)\alpha L_p}{\alpha^2 L_p^2 - 1} \right] \left[\frac{\frac{s_p L_p}{D_p} + \alpha L_p - \left(\frac{s_p L_p}{D_p} \cosh \frac{t'}{L_p} + \sinh \frac{t'}{L_p} \right) e^{-\alpha t'}}{\frac{s_p L_p}{D_p} \sinh \frac{t'}{L_p} + \cosh \frac{t'}{L_p}} - \alpha L_p e^{-\alpha t'} \right] \quad (3)$$

where

F_o is the incident photon flux

R is the reflection coefficient at the ITO/
CdTe interface

s_p is the recombination velocity at the ITO/
CdTe interface

L_p is the hole diffusion length

D_p is the hole diffusion constant

α is the absorption coefficient of CdTe

t' is the distance between the ITO contact and
the edge of the depletion region, i.e.,

$$t' = t - W.$$

Taking $S_p \rightarrow \infty$ and $t' \gg L_p$, Equation (3) simplifies to:

$$J_p = \frac{qF_o(1-R)\alpha L_p}{(1-\alpha^2 L_p^2)} \left[(1+\alpha L_p) e^{-\alpha t'} - 2e^{-t'/L_p} \right] \quad (4)$$

The drift component of the photogenerated current on the other hand can be obtained from the number of photogenerated carriers in the depletion region:

$$\begin{aligned} J_{dr} &= qF_o(1-R)\alpha \int_{t'}^t e^{-\alpha x} dx \\ &= qF_o(1-R) \left(e^{-\alpha t'} - e^{-\alpha t} \right) \end{aligned} \quad (5)$$

The total current density is the summation of two components, and it is given by the equation:

$$J_T = qF_0(1-R) \left\{ \frac{\alpha L_p}{1-\alpha^2 L_p^2} \left[(1+\alpha L_p) e^{-\alpha t'} - 2e^{-t'/L_p} \right] + e^{-\alpha t'} - e^{-\alpha t} \right\} \quad (6)$$

It is observed that Equation (6) can be plotted as a function of L_p if α , t' and t are known. Since the films are on ITO substrates, the measurement of the absorption coefficient (α) is easy. The film thickness (t) can be found by weighing the films or from interference patterns in the transmission spectra. The depletion region width can be obtained from capacitance measurements and t' can be found ($t' = t-w$).

These procedures are carried out for a solar cell of 0.8 μm thickness. The resulting theoretical curves are given in Figure 2. These curves were normalized with respect to the peak value. The corresponding experimental curve #2 is shown in Figure 3. Spectral response taken from the gold contact is also given in this figure. Comparing the theoretical and experimental results, one can estimate a diffusion length in the order of .05 - 0.1 μm for this solar cell.

This finding confirms that the assumption $t' \gg L_p$ was a valid one. The magnitude of the photogenerated current at small wavelengths also qualitatively confirmed the validity of this assumption.

More diffusion length measurements on several other devices are required to improve the statistical base.

Figure 1. Absorption Coefficient vs. Wavelength for Electrodeposited CdTe Films

Figure 2. Theoretical Curves Showing the Spectral Response for Different L_p 's. (Light Entering from ITO Contact)

Figure 3. Spectral Response of an ITO/n-CdTe/Au Solar Cell

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REFERENCES

1. H. O. McMahon, J. Opt. Soc. Am., 40, 376 (1950)
2. P. Rappaport and J. J. Wysocki, Acta Electronica, 5, 364 (1961)
3. R. O. Bell, Rev. Phys. Appl., 12, 391 (1977)
4. H. M. Brown and D. E. Brodie, Can. J. Phys., 50, 2502 (1972)
5. K. W. Mitchell, Ph.D. Dissertation, Stanford (1976)
6. Final Report "Emerging Materials for Solar Cell Applications - Electrodeposited CdTe," Monosolar, Inc., DOE Contract DE-ACO4-79ET23008 (1980)
7. J. J. Hovel, "Semiconductors and Semimetals - Solar Cells" ed. by W. Beer, Academic Press (1975)