Polycrystalline Thin-Film, Cadmium-Telluride Solar Cells Fabricated by Electrodeposition Cells

Final Subcontract Report 20 March 1992 – 27 April 1995

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Executive Summary

Objectives

The objective of this project was to develop improved processes for the fabrication of CdTe/CdS polycrystalline thin film solar cells. The technique we used for the formation of CdTe, electrodeposition, was a non-vacuum, low-cost technique that is attractive for economic, large-scale production.

Technical Approach

- (1) Optimization of CdTe electrodeposition conditions.
- (2) Improvement of the chemical bath deposition technique for CdS.
- (3) Optimization of CdCl₂ treatment and annealing processes and studies of recrystallization, interdiffusion, and residual stress resulting from heat treatment.
- (4) Investigation of ZnTe for improving the back contact and stability.

Results

Optimization of CdTe electrodeposition parameters. We have performed systematic investigations to optimize the growth conditions of CdTe. Among the parameters adjusted were the deposition potential, deposition current density, anode current ratio, water jet position, and Te concentration. High-quality CdTe films were consistently obtained as a result of this optimization effort.

Effect of CdCl₂ treatment and annealing on the microstructure and residual stress of the electrodeposited CdTe film. CdCl₂ treatment and subsequent annealing induce recrystallization and grain growth in electrodeposited CdTe. This recrystallization and grain growth were studied by examining changes in the X-ray diffraction (XRD) patterns. Specifically, the intensity ratio of the (220) peak and the (111) peak of the XRD pattern was used as a measure of the degree of texture in the film. With increasing annealing time, the crystalline orientation of the film moved toward a random state because of recrystallization. By monitoring the times required for 10% recrystallization, we obtained an activation energy of 2.5 eV for the recrystallization process.

We studied the annealing-induced stress in the electrodeposited CdTe based on XRD measurements. Heat treatment induces stress in CdTe films because of differences in the thermal expansion coefficients of CdTe and the substrates. For soda-lime glass substrates and the typical CdTe deposition conditions that yielded high efficiency solar cells, we observed a compressive stress in both the as-deposited and 410°C-annealed films. The magnitude of the compressive stress depended on the morphology of the CdS substrates. CdTe films deposited on CdCl₂-coated and annealed CdS substrates showed higher stress than films deposited on CdS that was not coated with CdCl₂. Interdiffusion at the CdS/CdTe interface and the formation of CdTe_{1-x}S_x was also observed by monitoring the changes in XRD lineshape.

Studies of Cu-doped ZnTe back contact layer. Cu-doped ZnTe was studied as a promising material for forming stable, low-resistance contacts to the p-type CdTe. The ZnTe was formed by vacuum

co-evaporation of Cu and ZnTe. The electrical properties were studied systematically as a function of Cu concentration and annealing temperature. The dark resistivity of the as-deposited ZnTe decreased by more than 3 orders of magnitude as the Cu concentration was increased from 4 to 8 atomic percent. The resistivity decreased to less than 1 ohm-cm after annealing at 260 °C for 30 min in vacuum. A decrease of conductivity was observed during annealing at 150 - 200 °C. The activation energy of the dark conductivity of annealed ZnTe was found to be less than 50 meV. The effect of ZnTe post-deposition annealing temperature and the types of metals used to contact the ZnTe on solar cell performances was studied. Application of the ZnTe as the back contact layer to our CdTe/CdS yielded cells with fill factors consistently exceeding 0.70 and energy conversion efficiencies consistently higher than 11%. The best cells we obtained showed a V_{oc} of 0.79 V, a J_{sc} of 20.8 mA/cm², an FF of 73.2%, and an efficiency of 12.1%. In terms of individual parameters, we have obtained a V_{oc} of over 0.8 V, and a FF of 74% on other cells.

Optimization of cell structures. We have investigated the effect of CdS thickness and annealing conditions on the resulting solar cells. We found that in addition to the possible changes of CdS films during annealing, the CdS film thickness may also affect the properties of the CdTe. The addition of a fresh, unannealed CdS layer on annealed CdS substrates was found to enhance the V_{oc} by an average of 50 mV. Effects of different types of conducting glass substrates have also been investigated.

3. Table of Contents

1.	Title Page	1
2.	Executive Summary	3
3.	Table of Contents	5
	List of Figures	6
	List of Tables	8
4.	Background	9
5.	Thin Film Deposition and Characterization	10
5.1	Thin Film Deposition and Solar Cell Fabrication Procedures	10
5.2	Characterization of CdS Thin Films	12
5.3	Annealing Studies of CdTe	17
5.4	ZnTe:Cu Thin Films for Back Contacts	27
5.5	Transparent Conducting Oxide Studies	33
5.6	Solar Cell Performances and Analysis	35
6.	Summary	42
7.	Acknowledgements	43
8.	References	44
9.	Appendices	46
8.1	Personnel	46
8.2	Laboratory Improvements	47
8.3	Publications	47

List of Figures

Figure 5.2.1. SEM micrographs showing the surface of our chemical bath deposited CdS films. The density of homogeneously deposited CdS particles on the surface is very low.

Figure 5.2.2. X-ray diffraction data for dip-coated CdS film deposited on SnO₂-coated glass.

Figure 5.2.3. X-ray diffraction data for dip-coated CdS film deposited on bare glass.

Figure 5.2.4. The three-point configuration we used for measuring the electrical resistivity of CdS films in the vertical direction.

Figure 5.2.5 SEM picture of the white spotted region of annealed CdS showing CdS grains and the overlying dendrites.

Figure 5.2.6. Raman scattering data for annealed, dip-coated CdS films on bare glass and on SnO₂-coated glass.

Figure 5.3.1. SEM (top-view) of the as-deposited (a) and annealed (b) CdTe films.

Figure 5.3.2. Cross-sectional SEM picture of the as-deposited (a) and annealed (b) CdTe films.

Figure 5.3.3. X-ray diffraction (XRD) patterns of different CdTe samples: annealed film, as-deposited film, and CdTe powders.

Figure 5.3.4. Normalized intensity ratios of XRD peaks for CdTe films annealed at various temperatures for different times. a: 344°C; b: 351°C; c: 361°C; d: 375°C.

Figure 5.3.5. Relationship between the annealing temperature and the time for 10% recrystallization.

Figure 5.3.6. Lattice constants of electrodeposited CdTe as a function of $\cos^2\theta/\sin\theta$.

Figure 5.3.7. Changes of lineshape of the high-angle XRD peak of CdTe films.

Figure 5.3.8. XRD patterns obtained from various CdTe films: (1) CdTe on as-deposited CdS, (2) CdTe on CdS annealed without CdCl₂ treatment, and (3) CdTe on CdS annealed with CdCl₂ treatment.

Figure 5.4.1 XRD patterns on as-deposited ZnTe:Cu/glass samples: (a) overdoped (#083193) and (b) lightly doped (#091493).

Figure 5.4.2. Relationship between grain sizes and deposition rate of ZnTe films on glass substrates.

Figure 5.4.3. Electrical resistivity of vacuum-evaporated ZnTe films on glass as a function of Cu

concentration: (a) as-deposited and (b) after annealing at 260°C for 30 min in vacuum.

Figure 5.4.4. The conductivity vs. temperature measurements. Curve 1 was measured while ramping the temperature to the annealing temperature and curve 2 was measured after the sample was cooled.

Figure 5.4.5 The activation energy of dark conductivity of ZnTe films deduced from temperature dependence between 20-120°C. open as-deposited; solid annealed at 260° C.

Figure 5.4.6. The dark conductivity of ZnTe films as a function of temperature.

Figure 5.4.7. XRD patterns of electrochemically deposited ZnTe film.

Figure 5.6.1. $1/C^2$ vs V plots of high efficiency (10-11%) cells (a) and medium efficiency (8 - 9%) cells (b).

Figure 5.6.2. $1/C^2$ vs V plots of CdS/CdTe/ZnTe cells (a) using Au and Ni as contact metals to ZnTe.

Figure 5.6.3. Light I-V curve (measured at NREL) of a CdS/CdTe/ZnTe/Au cell showing 12.1% efficiency.

Figure 5.6.4. The diode forward current ($J + J_{sc}$) as a function of the bias across the junction ($V - JR_s$). The illumination intensity was 100 mW/cm².

List of Tables

Table 5.3.1. Full-width at half maximum (FWHM) values of XRD peaks of as-deposited CdTe films (#051394) electrodeposited on various CdS samples.

Table 5.3.2. Comparison of the lattice parameters (in Å) of different CdTe samples estimated from the XRD peak positions.

Table 5.6.1. Performance parameters of CdS/CdTe/Au solar cells as a function of CdTe annealing time at 350°C.

Table 5.6.2. Effect of CdS thickness on CdS/CdTe cell performances.

Table 5.6.3. Effect of CdS dual-layer on CdS/CdTe cell performances

Table 5.6.4. Effect of ZnTe annealing temperature and back contact metal on cell performances.

Table 5.6.5. Progress in cell performances (measured by NREL) for CdTe/CdS cells fabricated at CSM.

4. Background

As described in the Solicitation (LOI NO. RM-1-11036) which led to this contract, polycrystalline thin-film CdTe photovoltaics are considered among "the leading thin-film materials in terms of efficiency and long-term reliability". Early companies prominent in the development of this technology have included Photon Energy and Ametek in the U.S., Matsushita in Japan, and British Petroleum in the U.K. In 1990, Ametek made a decision to abandon further development of CdTe photovoltaics and to donate all related assets (patents, laboratory know-how, and equipment) to the Colorado School of Mines Foundation. The Ametek facility was re-established at the Department of Physics of the Colorado School of Mines and formed the basis, along with the laboratory know-how, for the current work.

The Ametek research, supported to a large extent by NREL (SERI), led to solar cells of 11.2% efficiency [1-3]. Moreover, the unique, low cost electrodeposition methods used by Ametek for this material have attracted a great deal of interest. At the same time, additional research is still needed to improve upon the efficiencies and performance levels achieved to date. Among the significant issues are interface carrier recombination and top-layer photon absorption which presently limit the short-circuit current, junction recombination which limits the open-circuit voltage, and series-resistance losses which suppress the fill-factor.

The intent of the CSM contract was to build upon the Ametek experience and expertise regarding polycrystalline, thin-film, CdTe solar cells to improve certain processing steps and the potential for economic, large-scale production. Improved efficiencies were also a major goal. High-quality film growth techniques, materials analysis, device characterization, and device fabrication have all been of particular interest in our work.

5. Thin Film Deposition and Characterization

5.1. *Thin Film Deposition and Solar Cell Fabrication Procedures*

The system we investigated consisted of electrodeposited CdTe on chemical-bath-deposited CdS on SnO₂-coated sodalime glass substrates (Nippon Sheet Glass). The transparent conducting SnO₂ substrates had a sheet resistance of 10Ω/sq. The substrate size was 5 cm x 7.5 cm for both the CdS and CdTe deposition. The CdS layers (0.1 - 0.3 μm thick) were deposited by chemical bath deposition (CBD). The CdTe layers (2 μm thick) were deposited electrochemically from an aqueous solution containing CdCl₂ and TeO₂. CdCl₂ mist treatment and subsequent annealing were performed following both the CdS and CdTe deposition. The highest annealing temperature during the cell processing did not exceed 450°C. Prior to the deposition of the back contact, the CdTe was etched in Br₂-MeOH. The back contact layers were either Au, without a Cu interlayer, or Cu-doped ZnTe. In the latter case, the Cu content was kept low so that the total equivalent thickness of Cu was less than 1 nm.

Cadmium sulfide films were deposited by a chemical bath deposition (CBD) method [4]. The solution was made from cadmium salts (CdSO₄, CdAc₂, CdCl₂, etc), an organic sulfur-containing reducing agent (Thiourea, NH₂CSNH₂ or thioacetamide, NH₂CSCH₃), and ammonia. CdS occurs when the ionic product of [Cd⁺²] and [S⁻²] exceeds the solubility product (K_{sp}) of CdS. Even though the solubility product of CdS is very low (about 1.4 x 10⁻²⁹), the precipitation of CdS can take place easily. In order to avoid excessive precipitation, the preparation of CdS thin films should be based on the slow release of Cd⁺² and S⁻² in solution. The concentrations of Cd⁺² and S⁻² were adjusted to just barely exceed the solubility product of CdS. In this case, the nucleation and growth of CdS films occurs by ion-by-ion condensation. Slow release of the Cd⁺² ions was achieved by the dissociation of a complex species of cadmium. The S⁻² ions were introduced by decomposition of thiourea in alkaline solution.

Two types of solutions were used in our study. One reaction mixture was composed of CdAc₂ (10⁻³M), NH₄Ac (0.02M), NH₄OH (0.4M), and (NH₂)₂CS (5 x 10⁻³M) in an aqueous solution⁷, with a pH value of about 9. The mixture was warmed from room temperature to about 82°C under constant stirring. The nucleation of CdS started after about 10 min. CdS thin films were then deposited on SnO₂-coated glass substrates to a thickness of about 1000Å in 50 min. The average deposition rate was about 25Å/min with a concentration ratio of [CdAc₂] to [(NH₂)₂CS] of about 1/5. The second reaction mixture was composed of CdSO₄ (1.5 x 10⁻³M), NH₄OH (1.8M), and (NH₂)₂CS (1.5 x 10⁻¹M) or (NH₂)₂CS (1.5 x 10⁻²M) in an aqueous solution, with a pH value of about 11. The nucleation of CdS started after about 2.5 min for (NH₂)₂CS (1.5 x 10⁻¹M) or after about 3.0 min for (NH₂)₂CS (1.5 x 10⁻²M). CdS thin films were deposited on SnO₂-coated glass substrates at a rate of about 1000Å in 20 min. The average deposition rate was about 50Å/min at a concentration ratio of [CdSO₄] to [(NH₂)₂CS] between 0.01 and 0.1.

The CdS films were annealed before the electrodeposition of CdTe. For this purpose, a CdCl₂ coating was applied to the surface of the CdS using a mist generator containing a 2.4 M CdCl₂ aqueous solution. A Devilbis™ ultrasonic nebulizer generated the mist which was carried

though a tube to a preheated ($\sim 150^{\circ}\text{C}$) box where the sample was placed. After the CdCl_2 treatment, the sample was annealed at 450°C for 50 min in a N_2 atmosphere and cooled in the furnace. Prior to the CdTe electrodeposition, the CdS substrates were rinsed in hot ($\sim 80^{\circ}\text{C}$) DI water and dried in N_2 . Electrical leads were connected to the edges of the substrates using indium solder.

The CdTe deposition was done in an electroplating system [5] composed of four electrodes: Cd and Te anodes, a Ag/AgCl reference electrode, and a cathode (sample substrate). The deposition current J_{dep} was controlled by adjusting the concentration of the tellurium ions [Te]. The experimental parameters that may affect the film's properties are: the deposition current density J_{dep} , the deposition current ratio between the Te anode and the Cd anode $J_{\text{Te}}/J_{\text{Cd}}$, the deposition potential V_{dep} , the pH of the solution, the concentration of the Cd and Te ions in the solution [Cd] [Te], the deposition temperature T_{dep} , and the degree of agitation. The optimized CdTe deposition conditions were: pH, 2; temperature, 80°C ; 1.2 M CdCl_2 ; J_{dep} between 0.26 and 0.40 mA/cm^2 ; deposition potential -600 mV (vs. Ag/AgCl electrode); [Te], 20~22 ppm; and anode current ratio, $J_{\text{Te}}/J_{\text{Cd}}$, close to 2.0. A typical growth rate was $1 \mu\text{m/hr}$ and the Coulomb efficiency of the deposition process was 85~90%. After completion of the deposition, the CdTe samples were rinsed in hot DI water and dried in N_2 .

For the annealing of the CdTe, a CdCl_2 coating was applied to the CdTe surfaces using the same procedure as used for the CdS layers. The samples were annealed at 410°C for 45 min in air, removed from the furnace, and cooled in ambient to room temperature. Etching of the CdTe back surface was done immediately before the back contact metallization by dipping the samples in 0.1% Br-MeOH for 10 s. Back contacts were made by evaporating Au or Cu-doped ZnTe thin films (discussed in 5.4). In the latter case, the Cu content was kept low so that the total equivalent thickness of Cu was less than 1 nm.

Our characterization studies of CdS included optical transmission, thickness measurement by alpha-step profilometry and ellipsometry, electrical resistivity and the related activation energy, x-ray diffraction (XRD), scanning electron microscopy (SEM), scanning-tunneling-microscopy (STM), Raman scattering, and small-angle x-ray scattering (SAXS). The characterization of CdTe thin films, both as-deposited and annealed, included SEM, XRD, SAXS, and electrical measurements. SEM was performed using a JEOL Model 840 instrument. The XRD measurements were performed in a Rigaku x-ray diffractometer using $\text{CuK}\alpha$ radiation. Small scanning steps ($\Delta 2\theta = 0.02^{\circ}$ or 0.01° per step) and fixed time intervals of either 2 s or 1 s for each step were used. A wide range of 2θ (from 20° to 80° or 20° to 100°) was scanned, so that all the major diffraction peaks could be detected.

5.2. Characterization of CdS Thin Films

The surface morphology of CdS has been greatly improved by modifying the deposition procedure. As is shown in Figs. 5.2.1, the density of "homogeneously nucleated particles" adsorbed on the surface is very low in the films. This is critical for improving the large-area uniformity of the final CdS/CdTe cells. The surface particles may become shunt paths if they dislodge before or during the subsequent CdTe deposition.

Figure 5.2.1. SEM micrographs showing the surface of our chemical bath deposited CdS films. The density of homogeneously deposited CdS particles on the surface is very low.

Figures 5.2.2 and 5.2.3 show XRD patterns of the CdS films. The films were typically annealed in nitrogen for 50 minutes at a temperature of 450°C after a dip coating of CdCl₂. For CdS deposited on both bare glass and SnO₂-coated glass, we observed similar results: (1) the as-deposited CdS consisted of a small grain-size hexagonal (h) or cubic (c) structure (there was some overlap between the CdS (002) peak and the SnO₂ (110) peak) with a strong preferred orientation of the (002) [h] or (111) [c] grains parallel to the film surface; (2) the annealed CdS was clearly the hexagonal structure with a near-random grain orientation. The crystallinity of the CdS film on SnO₂ was found to be better than that on bare glass, based on a close examination of the width of XRD peaks.

Figure 5.2.2. X-ray diffraction data for dip-coated CdS film deposited on SnO_2 -coated glass.

Figure 5.2.3. X-ray diffraction data for dip-coated CdS film deposited on bare glass.

Figure 5.2.4. The three-point configuration we used for measuring the electrical resistivity of CdS films in the vertical direction.

The electrical resistivity of the CdS layer was measured. Instead of measuring the lateral resistivity, we measured the CdS resistivity in the vertical direction. This resistivity is expected to be quite different from the lateral resistivity because of the columnar structure of the CdS. It is also more relevant to the cell processing and performance. Such resistivity measurements are, however, difficult to perform because the CdS film is very thin. The sheet resistance of SnO_2 is of the same order as the resistance across the $0.3 \mu\text{m}$ CdS film. We used a three-point measurement configuration (Fig.5.2.4) to suppress the contribution from SnO_2 . The dark resistivity value we obtained using this method is $1 \times 10^4 \text{ ohm-cm}$. This value falls near the low end of the resistivity (lateral) range reported by Chu [6] for chemical-bath-deposited CdS. The resistivity measured under illumination (100 mW/cm^2), however, showed only a reduction by a factor of two. This is much smaller than the photoconductivity ratio of 50 - 1000 reported for lateral conductivity. The relatively large resistivity we measured under illumination was most likely caused by the contact resistance between the Al electrode and CdS. The resistivity we measured in the dark was not expected to be affected by the contact resistance because of the high value of the CdS dark resistivity.

The annealing with CdCl_2 treatment sometimes left white spots, with sizes ranging from about 0.5 mm to 5 mm , on the CdS films. Films annealed without CdCl_2 treatment did not show this feature. These spots are actually conglomerates of dendritic patterns of either Cd metal or some Cd-rich phase, as is indicated by energy dispersive x-ray spectroscopy (EDS) measurements made on the normal CdS and on the white spots. Fig. 5.2.5 is an SEM picture of the white spotted region showing both the dendrites and the underlying CdS grains. A possible mechanism for the formation

of this pattern is either the uneven coating of CdCl_2 or Cd vapor transport from elsewhere on the surface to localized nucleation sites. In terms of device performance, the white spots may act as shunt paths or blocking barriers, depending on the nature of the junctions formed with the CdS layer and subsequently with the CdTe layer, and thus cause poor cell performance.

Fig. 5.2.5. SEM picture of the white spotted region of annealed CdS showing CdS grains and the overlying dendrites.

The Raman scattering technique was used to characterize the CdS thin films. A well-crystallized, large CdS single crystal exhibits an LO peak at $\sim 301 \text{ cm}^{-1}$. As the crystalline size becomes smaller, the LO peak position down-shifts and its width becomes broader⁸. Therefore, we can use Raman scattering to probe the crystallite size and the quality of CdS thin films. Figure 5.2.6 shows Raman spectra taken from CdS thin films deposited on SnO_2 and Corning 7059 glass substrates and annealed at 450°C for 50 min. The peak position from the D31-2 sample deposited on 7059 glass was lower by $\sim 1 \text{ cm}^{-1}$ than that of the D31-4 sample deposited on SnO_2 . Also note that the Raman peak width of the D31-2 sample was broader. This indicates that the CdS film on SnO_2 may be better crystallized and have larger grain size than the film on the glass substrate. STM work discussed in our earlier report [7] shows that much larger grain sizes were found for the CdS films on SnO_2 substrates. Luminescence from CdS films when irradiated with a $5145 \text{ \AA}$ laser beam also appears to be correlated to the crystallinity. The amount of luminescence from annealed CdS films was found to be two-orders-of-magnitude larger than that of unannealed films.

Figure 5.2.6. Raman scattering data for annealed, dip-coated CdS films on bare glass and on SnO₂-coated glass.

5.3. Studies of CdTe Annealing

SEM images of both the as-deposited and the annealed CdTe films were taken. The as-deposited CdTe films had a faceted morphology as shown in Figure 5.3.1. This is usually a sign of high crystallinity. The cross-sectional SEM picture (Figure 5.3.2) reveals that the as-deposited films had a dense, columnar structure. Films annealed with CdCl₂ coating showed much larger grain size.

We used X-ray diffraction to study the recrystallization of CdTe during annealing. The XRD patterns of the as-deposited and annealed CdTe films are shown in Figure 5.3.3. For comparison, the XRD pattern of CdTe powder is also shown. The intensities of the CdTe peaks show strong preferred orientation of the grains such that the (111) planes (corresponding to strongest peak in all plots) were parallel to the film surface in the as-deposited film. Upon annealing, a transition to a near-random texture occurred, as evidenced by the resemblance of the XRD patterns of the annealed films to that of the powder. The decrease in intensity of the (111) peak upon annealing suggests that new grains with the different orientations grew at the expense of the (111) grains oriented parallel to the surface. The degree of the recrystallization in CdTe can be quantified using the ratio (R) between the (220) and the (111) XRD peak intensities. This ratio can be normalized by dividing it with the same ratio obtained from CdTe powders to obtain the "normalized intensity ratio" (R_n), i.e.,

$$R = I(220)/I(111) \quad (1)$$

$$R_n = R_{\text{film}} / R_{\text{powder}} \quad (2)$$

R_n is a measure of the degree of texture in a film as referenced to that of powder. For example, $R_n = 0$ means that the film is completely textured along $\langle 111 \rangle$, and $R_n = 1$ indicates completely random orientation, assuming that the powder sample had random grain orientation.

Fig.5.3.4 shows R_n as a function of annealing time at several annealing temperatures. Prior to annealing, the CdTe films were coated with a thin layer of CdCl₂ powder. For all annealing temperatures studied, R_n increased with annealing time, indicating that the orientation of the crystallites became more randomized as a result of recrystallization. A quantitative analysis of the recrystallization was performed by choosing an arbitrary value of R_n (0.1 in our case, indicated by the horizontal line in Fig.5.3.4) and monitoring the time τ required to reach this ratio at various annealing temperatures [8]. The characteristic time τ is inversely proportional to the recrystallization rate and, when plotted as a function of inverse temperature, shows typical Arrhenius behavior (Fig. 5.3.5). Using the equation:

$$1/\tau = A \exp (- E_a / kT) \quad (3)$$

We obtained an activation energy (E_a) of 2.5 ± 0.3 eV for the recrystallization process. In general, the recrystallization process involves both nucleation and subsequent grain growth. The observed activation energy for recrystallization may contain contributions from both steps. Therefore, we can only use E_a for an estimation of an upper limit for the activation energy of grain growth. A correlation between the activation energy of grain growth with the activation energy of atomic diffusion at grain boundaries requires a better knowledge of the grain growth mode.

(a)

(b)

Figure 5.3.1. SEM (top-view) of the as-deposited (a) and annealed (b) CdTe films.

(a)

(b)

Figure 5.3.2. Cross-sectional SEM picture of the as-deposited (a) and annealed (b) CdTe films.

Figure 5.3.3. X-ray diffraction (XRD) patterns of different CdTe samples: annealed film, as-deposited film, and CdTe powders.

Figure 5.3.4. Normalized intensity ratios of XRD peaks for CdTe films annealed at various temperatures for different times. a: 344°C; b: 351°C; c: 361°C; d: 375°C.

Figure 5.3.5. Relationship between the annealing temperature and the time for 10% recrystallization.

We have also performed XRD studies of CdTe samples annealed without the application of a CdCl₂ coating. In this case, the value of R_a increased much more slowly with annealing time, even for a relatively high annealing temperature (400°C), indicating that CdCl₂ coating plays a critical role in facilitating the recrystallization process. An activation energy for the recrystallization in the absence of CdCl₂ could not be reliably determined in the temperature range studied here.

We measured the lattice constants of the CdTe thin films using XRD to assess the residual stress. The lattice constants were measured along the direction normal to the sample surface when using a standard $\theta/2\theta$ diffractometer. A decreased lattice constant in the surface normal direction is a result of an increase of in-plane lattice spacing which in turn is a result of an in-plane tensile stress and vice versa for an in-plane compressive stress. For reference, we measured the lattice constants of commercial CdTe powders and CdTe single crystals. Notice that the differences in lattice constant we are concerned with here are rather small. In order to detect this difference unambiguously, we exercised caution to eliminate common systematic errors in powder diffractometry. Each diffraction peak was fitted with a superposition of $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks (Pearson VII peak shape function) to accurately extract the $K_{\alpha 1}$ position. The plane spacing was then obtained using $\lambda(K_{\alpha 1}) = 0.154056$ nm. Each lattice constant value was obtained by plotting the lattice constant derived from each diffraction peak as a function of $\cos^2\theta/\sin\theta$ with extrapolation to $\theta = \pi/2$ by a least square fit (Figure 5.3.6). Both reference materials (the data for the single crystal are not shown) show a lattice constant of 0.6481 nm, in good agreement with literature values [9]. Both the as-deposited and 410°C-annealed CdTe films show larger lattice constants normal to the thin film in comparison to the powder value. This indicates an in-plane compressive stress, caused by the lattice mismatch between CdS and CdTe and the difference in thermal expansion coefficients between the thin films and the glass substrates. Based on the measured difference between the lattice constants of CdTe films and powders, we estimated the residual stress in the CdTe thin films to be 30 MPa, using the known elastic constants of CdTe. We have scraped off the CdTe thin film from the glass substrate and performed XRD measurement on the collected powders (Figure 5.3.7). The lattice parameters of CdTe decrease and approach the value of the commercial CdTe powder. This result indicates that the larger lattice parameter we observed with the thin films is indeed a result of the different thermal expansions between the thin films and glass substrates.

In addition to the changes in lattice parameter, we also observed changes in the XRD lineshape for CdTe films annealed at 410°C. This is shown in Fig.5.3.7. The XRD pattern is composed of two sets of peaks. One set of peaks corresponds to CdTe. The second set, characterized by a smaller lattice parameter and growing in intensity with annealing time, indicates the formation of CdTe_{1-x}S_x [10]. Based on the observed difference in lattice parameter and the known lattice constants of CdTe (0.6481 nm) and CdS (0.5818 nm), we estimate the content of S in CdTe to be about 3%. We have also monitored the XRD lineshape of the CdS to investigate the possible diffusion of Te into CdS and the formation of CdS_{1-y}Te_y. For this purpose, the CdTe layer was etched off after annealing, using chromic acid. No distinct changes in XRD lineshape were observed. However, the CdS film that was annealed in contact with CdTe dissolved at a much higher rate in chromic acid than the CdS that was annealed alone, suggesting the occurrence of

Figure 5.3.6. Lattice constants of electrodeposited CdTe as a function of $\cos^2 \theta / \sin \theta$.

Figure 5.3.7. Changes of lineshape of the high-angle XRD peak of CdTe films.

interdiffusion in the former case. These results indicate that the composition of the CdS layer was changed uniformly across the film by the annealing process.

We studied the effect of CdS substrates on the microstructure of the CdTe films. Three different types of chemical-bath deposited CdS were used. All three types of CdS substrates had "dual structure", i.e., annealed underlayer plus different types of overlayer such as: (1) as-deposited (#1), (2) annealed without CdCl₂ (#2), and (3) annealed with CdCl₂ treatment (#3). Annealing with and without CdCl₂ resulted in different microstructure and surface morphology in the CdS, which in turn affected the morphology of the CdTe films. The XRD patterns of CdTe films grown on these 3 types of CdS substrates are shown in Figure 5.3.8. Sample#1 shows XRD peaks not as well defined as those from the other two samples. The full-width at half maximum (FWHM) of the peaks were estimated and listed in Table 5.3.1. From the FWHM values, it is clear that sample#3 had the best crystallinity and largest grains. The lattice parameters of annealed CdTe also showed a dependence on the types of CdS films. The values are listed in Table 5.3.2 along with the value from bulk CdTe powder as a standard. The larger lattice parameters of these films in comparison with that of CdTe powder indicate that all the films were under compressive stress. Sample#3 had the largest lattice parameter measured along the direction normal to the film, indicating the largest in-plane stress among the three. The high compressive stress in sample#3 suggests that it had the most compact microstructure. Solar cells fabricated with CdTe deposited on substrates of type #3 showed typically higher efficiencies than cells using the other 2 types of CdS substrates.

Table 5.3.1. Full-width at half maximum (FWHM) values of XRD peaks of as-deposited CdTe films (#051394) electrodeposited on various CdS samples.

Index of plane	2 θ , degrees	Sample#1 FWHM	Sample#2 FWHM	Sample#3 FWHM
220	39.35	0.33	0.24	0.24
311	46.47	0.33	0.31	0.20
331	62.49	1.4	1.3	0.73
422	71.00	0.73	0.63	0.51
333	76.23	0.27	0.25	0.26

Table 5.3.2. Comparison of the lattice parameters (in Å) of different CdTe samples estimated from the XRD peak positions.

	As-deposited	Annealed
Bulk Powder	6.481	
Sample#1		6.484
Sample#2	6.489	6.486
Sample#3	6.500	6.487

Figure 5.3.8. X-ray diffraction (XRD) patterns obtained from various CdTe films: (1) CdTe on as-deposited CdS, (2) CdTe on CdS annealed without CdCl_2 treatment, and (3) CdTe on CdS annealed with CdCl_2 treatment.

5.4. Cu-Doped ZnTe Thin Films for Back Contacts

ZnTe films doped with Cu were made by vacuum evaporation at a pressure of 1×10^{-6} torr. The vacuum system was partitioned into two sections; one for a ZnTe powder source and the other for a Cu source. The ZnTe and Cu deposition rates were measured by separate thickness monitors. The substrates were held at room temperature during deposition. Post-deposition annealing was performed in vacuum or in a N_2 environment. The electrical properties of the ZnTe films were studied for the following deposition and annealing conditions:

- i) atomic concentration of Cu between 0 and 10%;
- ii) ZnTe:Cu layer thickness between 50 and 120 nm;
- iii) post-deposition annealing temperature in the range of 150 and 260°C.

We found that it is highly critical to pretreat the ZnTe source materials carefully before they are used for thin film depositions. Even high purity ZnTe powders (nominally 5N, obtained from several vendors) may contain up to several percent of metallic Te. Such metallic Te may produce Te secondary phase in the deposited ZnTe films. Overdoping with Cu may also cause the formation of $CuTe_x$ secondary phase. With proper control of the deposition conditions, ZnTe films free of any secondary phase can be obtained. The XRD pattern of such a film is shown in Figure 5.4.1. From the linewidth of the XRD peaks, we estimated the average grain size of the ZnTe, using Scherrer's formula. The results are shown in Figure 5.4.2. As can be expected, larger grains were obtained at lower deposition rates.

Fig. 5.4.1. XRD patterns on as-deposited ZnTe:Cu/glass samples: (a) overdoped (#083193) and (b) lightly doped (#091493).

Fig. 5.4.2. Relationship between grain sizes and deposition rate of ZnTe films on glass substrates.

The electrical properties of the vacuum evaporated ZnTe films, both undoped and Cu-doped, were investigated. Fig. 5.4.3 (a) shows the change of the electrical resistivity (ρ) of as-deposited ZnTe films with different Cu contents [Cu]. The Cu concentrations in the plot are the values obtained from the thickness monitors. Considering the fact that the sticking coefficients of both ZnTe and Cu on room temperature substrates should be close to one, these nominal Cu concentrations should be close to the actual values. Auger electron spectroscopy measurements also confirmed this point. As shown in Figure 5.4.3, the resistivity ρ of the ZnTe film decreased with increasing [Cu] until it reached saturation at about $5 \times 10^{-3} \Omega \text{ cm}$. After annealing at 260°C for 30 min in vacuum, ρ decreased dramatically, as a result of the activation of Cu dopants. The charge carrier mobility may also be increased as a result of decreased intragrain crystalline defects and of grain growth. A large change in ρ was observed after annealing for films with [Cu] below 8 at.%, whereas only a small change occurred in samples with [Cu] above 8 at.%. This change in resistivity with Cu concentration is consistent with previous studies by the Ametek group [3]. The drastic decrease of resistivity at the annealing temperature of 260°C is also consistent with the results of Gessert et al. [11].

The conductivities of the films were measured at different temperatures in order to estimate the activation energy. A typical result of the conductivity vs. temperature measurements is

Fig. 5.4.3. Electrical resistivity of vacuum-evaporated ZnTe films on glass as a function of Cu concentration: (a) as-deposited and (b) after annealing at 260°C for 30 min in vacuum.

Fig. 5.4.4. The conductivity vs. temperature measurements. Curve 1 was measured while ramping the temperature to the annealing temperature and curve 2 was measured after the sample was cooled.

presented in Fig.5.4.4. Both as-deposited and annealed samples showed the predicted behavior, i.e. a linear $\log(\sigma)$ vs. $1/T$ relationship. For undoped ZnTe, the conductivity vs temperature curves show reversible behavior (Fig. 5.4.4). Consequently, identical room temperature conductivity and activation energy were obtained for the as-deposited and annealed films. For Cu-doped films, however, the conductivity underwent irreversible changes as a result of annealing. Both the room temperature conductivity and the activation energy were different for as-deposited and annealed films. The activation energies estimated from the slopes of the curves are plotted in Fig. 5.4.5 for as-deposited samples (a) and for annealed samples (b). The activation energy E_a decreases with increasing [Cu]. After annealing, this dependence of E_a on [Cu] became weaker. In all cases, the activation energy of these films depended on the final annealing temperature. For films annealed at $>240^\circ\text{C}$, the activation energy was less than 50 meV.

Fig. 5.4.5. The activation energy of dark conductivity of ZnTe films deduced from temperature dependence between 20 – 120°C . open: as-deposited; solid: annealed at 260°C .

Figure 5.4.6 shows the electrical conductivity (dark) of a Cu-doped ZnTe film as a function of annealing temperature. The irreversible change of conductivity as a result of annealing is evident. The sheet resistance of the as-deposited ZnTe film was typically $6000 \Omega/\text{sq}$. The conductivity increased with increasing temperature for annealing temperatures below 130°C , as is commonly expected. At medium annealing temperatures (between 150° to 200°C), a decrease of conductivity was observed. Annealing at higher temperatures ($>240^\circ\text{C}$) led to the recovery and further increase of conductivity. Dark I-V, two-point and four-point probe methods all yielded the same result, indicating that the abnormal decrease of conductivity at 150 - 200°C annealing temperature is a genuine phenomenon; however, its physical origin is not clear.

Fig. 5.4.6. The dark conductivity of ZnTe films as a function of temperature.

Fig. 5.4.7. XRD patterns of electrochemically deposited ZnTe film.

We have also investigated the electrodeposition of ZnTe thin films using a procedure similar to that reported by Mondal et al. [12]. Samples were grown under potentiostatic control in a solution of 1 M ZnSO₄, saturated with TeO₂. A variety of cathode potentials was explored. Analyses were conducted on samples grown at -1.1 V_{sce}, for 4 hr. This condition yielded a deposition current density of about 0.3 mA/cm². The XRD results showed that, prior to annealing, there was a large amount of elemental Te. During an annealing step (425 °C, in air) the Te in the electrodeposited layer nearly disappeared, and cubic ZnTe was formed. Figure 5.4.7 shows XRD data of our ZnTe films formed by the electrochemical process. A single phase cubic ZnTe was obtained. The unreacted Te phase that was present in the as-deposited film (not shown in the Figure) was eliminated as a result of annealing.

5.5. *Transparent Conducting Oxide Studies*

One of the tasks of this contract was to investigate the properties of ZnO films deposited by ion-sputtering. This effort was undertaken by a graduate student, Mr. Yi Qu, who worked in close collaboration with scientists at NREL. The structural, electrical and optical properties of undoped and Al-doped ZnO films were studied under this task. XRD measurements revealed that the grain size increased with film thickness and deposition temperature. The largest size was found to be ~100 nm. For deposition temperatures higher than 250°C, the grain size saturated at this value. This led to changes in the electrical properties as the film thickness and deposition temperature changed. For a fixed film thickness for deposition temperatures exceeding 250°C, the resistivity did not change much with deposition temperature, but remained sensitive to film thickness because of the resistance associated with grain boundaries.

The electrical resistivity of undoped ZnO thin films was determined using both Hall measurements and a 4-point probe. Undoped ZnO films had a wide range of resistivity from $\sim 10^{-3}$ - 10^7 Ω -cm depending on deposition condition and film thickness. Hall measurements were carried out for films with resistivity lower than 10^2 Ω -cm. For films with resistivity higher than 10^2 Ω -cm, Hall measurements could not be made because of the difficulty involved in passing a current through such resistive layers. For the latter the resistivity was obtained through the relation $\rho = R_s t$, where R_s is the sheet resistance measured using a 4-point probe and t is the film thickness. Films deposited in a mixture of Ar and H₂ showed a low resistivity of 10^{-3} - 10^{-2} Ω -cm. In this case, the carrier concentration of as-deposited films could be as high as 10^{20} cm⁻³. However, the resistivity was not stable in this case, increasing with the exposure time (over a period of days) in air. Films deposited in a mixture of Ar and O₂ showed a high resistivity of more than 10^2 Ω -cm. Information about carrier concentrations and mobilities is not available in this case because of difficulties in performing Hall measurements. Films deposited in pure Ar showed medium resistivity of 10^{-1} - 10^2 Ω -cm. These films had a carrier concentration of 10^{17} - 10^{19} cm⁻³ and mobility of 1-25 cm²/V-s depending on film thickness and deposition temperature.

Undoped ZnO films deposited in a mixture of H₂ and Ar were used to study the effect of H₂ on the electrical properties. The results showed that the resistivity decreased dramatically when a small amount of H₂ was introduced into the deposition chamber. When more H₂ was added, the resistivity decreased more slowly and eventually leveled off. Hall measurements showed that the rapid decrease of resistivity was due to increases in both carrier concentration and mobility. However, the resistivity was not stable as mentioned earlier. When these films were exposed in air, even at room temperature, the resistivity increased. After about three weeks, the resistivity reached values comparable to those of films deposited in pure Ar.

Electrical and optical properties of as-deposited, ion-beam-sputtered ZnO:Al films were studied as a function of film thickness and doping concentration. Hall measurements revealed a general decrease in the bulk electrical resistivity with increasing film thickness. With an increase in film thickness from 100 to 200 nm, a significant decrease in resistivity from 2.8×10^{-2} to 4.4×10^{-3} Ω -cm was attributed to increases in both carrier concentration and Hall mobility. For thicker films, the resistivity was relatively insensitive to film thickness and approached a value of $\sim 8.6 \times 10^{-4}$ Ω -cm at a thickness of 1,100 nm. In this thickness regime, the slight decrease in

resistivity with increasing film thickness was attributed to an increase in carrier concentration alone. The above observations suggest the presence of at least two scattering mechanisms. It is speculated that grain boundary scattering and ionized impurity scattering are most likely.

Both undoped-ZnO and Al-doped ZnO (ZnO:Al) films were employed in the fabrication of CIS and CIGS solar cells. In these devices, the ZnO films were deposited using a pure ZnO target at room temperature with a thickness of $\sim 500\text{\AA}$. The ZnO:Al films were deposited to a thickness of $\sim 3000\text{\AA}$ using an Al-doped target at a temperature of 100°C . A CIGS solar cell with a structure of glass/Mo/CIGS/CdS/ZnO:Al/Ni/Al/MgF₂ fabricated at NREL achieved a record efficiency of 15.9% with the employment of the high quality ZnO and ZnO:Al films during the course of this project. Quantum efficiency measurements on this cell showed that even though high efficiency had been achieved, some increase in efficiency is still possible by reducing absorption in the window layers. Because absorption in the near-infrared (NIR) is caused by free carriers, improvement of the structural properties of the film will be important. The carrier concentration can be reduced with improvement of carrier mobility without worsening the electrical conductivity. This approach should lead to a reduced free carrier absorption in the NIR range.

Structural, electrical and optical measurements were also performed on films deposited on Corning 7059 glass substrates. The XRD results showed that the films have a highly preferred orientation with the c-axis perpendicular to the substrate. The electrical resistivities were $\sim 1\text{-}10\ \Omega\text{-cm}$ (ZnO) and $2\text{-}4 \times 10^{-3}\ \Omega\text{-cm}$ (ZnO:Al), respectively. The optical transmission was 85-90% in the visible range. A detailed discussion of these results can be found in References [13,14].

5.6. Solar Cell Performances and Analysis

We monitored the variation of Au/CdTe/CdS solar cell performances during the initial stages of annealing in order to improve our understanding of the annealing process. Table 5.6.1 lists the cell performance parameters as a function of annealing time for the annealing temperature of 350°C. A close examination of this Table and the CdTe morphological changes observed with XRD (section 5.3) reveals that annealing improved the solar cell performances in several steps. During the first 5 min, the main effect of annealing on CdTe was type conversion [15]. Even though the annealing temperature was rather low, a 5 min anneal was sufficient to result in an appreciable V_{oc} , indicating that the CdTe type conversion had already occurred. At this stage of annealing, recrystallization and grain growth were both negligible. For annealing times between 5 and 20 min, recrystallization was the dominant process. During this period, the most apparent improvement in cell performance was V_{oc} . J_{sc} and the series resistance were relatively unchanged. Presumably, the improvement of V_{oc} resulted from the passivation of recombination centers at the grain boundaries and partial elimination of deep levels associated with point defects. For longer periods (45 and 60 min) of annealing, grain growth dominated over recrystallization. Charge carrier recombination and series resistance associated with grain boundaries both decreased, leading to the enhancement of both J_{sc} and FF.

Table 5.6.1. Performance parameters of CdS/CdTe/Au solar cells as a function of CdTe annealing time at 350°C.

Time (min)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	dV/dJ at V_{oc} (ohm-cm ²)	Efficiency (%)
5	0.56	19.4	0.49	8.7	5.3
20	0.66	18.0	0.54	10.1	6.4
45	0.68	21.0	0.55	8.5	7.9
60	0.69	22.3	0.59	5.7	9.0

The effect of CdS thickness on CdTe/CdS cells was studied. The results are shown in Table 5.6.2. CdS thickness affected the cell performances drastically. The major difference came from V_{oc} . No distinctive differences in J_{sc} and FF were observed. The series resistance was actually smaller for cells made from thin CdS, contributing to a slightly higher FF. C-V measurements indicated that the doping concentration of CdTe was much higher for cells using thin CdS (6×10^{15} cm⁻³). This effect of CdS thickness on CdTe doping concentration is interesting. We have compared the deposition current vs potential curves during CdTe electrodeposition. The results are identical for the 2 CdS substrates with different thicknesses. This suggests that the difference in doping concentration originated most likely from the annealing process.

Table 5.6.2. Effect of CdS thickness on CdS/CdTe cell performances

CdS thickness	V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	Efficiency (%)
130 nm	0.46	20.8	65.8	6.4
280 nm	0.74	21.9	64.5	10.5

The open-circuit photovoltage obtained with electrodeposition at low processing temperatures was in general lower than the V_{oc} values obtainable with techniques that involve

processing at higher temperatures [16]. To compensate for this limitation and to obtain higher V_{oc} , we have explored ways of modifying the cell structure. It is known that annealing of the CdS layer with a $CdCl_2$ coating is beneficial for the cell performance. During the annealing of CdS, recrystallization and grain growth occur which affect the crystalline quality of the subsequently deposited CdTe films. However, the stoichiometry of the CdS may change as a result of annealing. The CdS/CdTe interface may also be affected by the residuals from the $CdCl_2$ treatment. In order to obtain the benefits of annealing and still have a stoichiometric surface, we deposited a fresh, unannealed CdS layer on annealed CdS substrates. The results are shown in Table 5.6.3. In comparison to the cell fabricated without the dual-layer CdS structure (sample 120993), the addition of the fresh CdS layer enhanced the V_{oc} by an average of 50 mV. However, a slight decrease in J_{sc} was also observed. Further experiments need to be done to optimize the conditions to realize the full potential of this approach.

Table 5.6.3. Effect of CdS dual-layer on CdS/CdTe cell performances

Sample #	Dual CdS layer	V_{oc} (V)	J_{sc} (mA/cm ²)
2-60	yes	0.780	18.9
1-60-2	yes	0.768	20.9
1-60-1	yes	0.774	20.7
120993	no	0.722	21.3

C-V measurements were performed consistently to correlate the cell performance with the CdTe film properties. We noticed that our 10-11% cells are characterized by doping concentrations in the 10^{14} cm⁻³ range and trap densities in the low 10^{15} cm⁻³ range. Cells with lower efficiencies (8 - 9%), on the other hand, showed higher doping concentrations and trap densities (both in the range of $2 - 5 \times 10^{15}$ cm⁻³). Typical examples are shown in Fig.5.6.1. The doping concentration of the electrodeposited CdTe that produced 10-11% cells was in the same range as that of CdTe films produced with other methods (CSS and spray pyrolysis) [17].

We have conducted investigations on the choice of metals used for the contact to ZnTe. Most previous studies concerning the ZnTe back contact layer used Ni as the contact metal. However, in our investigation, we observed that the open-circuit photovoltage of the solar cell was critically dependent on the processing conditions if Ni was used as the contact metal. In many cases, V_{oc} often decreased after Ni deposition. In contrast, deposition of Au on the ZnTe/CdTe/CdS structure led to consistent improvement of V_{oc} . Several Cu concentrations and ZnTe annealing temperatures were used in this study. Overall, cells using Au/ZnTe back contacts showed higher efficiency than cells with Ni/ZnTe contacts. Table 5.6.4 shows the results for a set of data which correspond to a Cu concentration of 5.5 at. % in ZnTe. Each data point is the average value obtained from 5 dot cells. For each annealing temperature, the Au- and Ni-contacted cells were fabricated side-by-side on the same piece of ZnTe/CdTe sample. Only the final metallization step was different. The results are consistent among different runs of experiments for different Cu concentrations. The major difference comes from V_{oc} . Cells made with Au/ZnTe showed consistently higher V_{oc} than those with Ni contacts. The series resistances were comparable in both cases. The difference in FF originated mainly from the difference in V_{oc} . With regard to annealing temperature, cells annealed at the intermediate temperature (168°C) showed higher fill factors and higher efficiencies.

Figure 5.6.1. $1/C^2$ vs V plots of high efficiency (10-11%) cells (a) and medium efficiency (8 - 9%) cells (b).

Table 5.6.4. Effect of ZnTe annealing temperature and back contact metal on cell performances.

Back Contact	Annealing temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	Efficiency (%)
Au	155	0.77	21.6	0.72	11.9
Au	168	0.77	21.4	0.73	12.1
Au	185	0.76	20.2	0.68	10.4
Ni	155	0.65	22.8	0.65	10.5
Ni	168	0.68	23.1	0.70	11.1
Ni	185	0.70	22.4	0.67	10.5

Figure 5.6.2. $1/C^2$ vs V plots of CdS/CdTe/ZnTe cells using Au and Ni as contact metals to ZnTe.

In order to understand the mechanism that leads to the observed difference in cell performances, we performed C-V measurements on these samples. As shown in Figure 5.6.2, cells with Ni/ZnTe back contacts showed Mott-Schottky behavior that is typical of a p-i-n cell [3]. At zero bias, the depletion layer width was comparable to the CdTe film thickness. The slope in the forward bias region yielded doping concentrations in the low 10^{14} cm⁻³ range. Cells with Au/ZnTe showed higher doping concentrations (in the range of 2×10^{15} cm⁻³). This higher doping concentration may have contributed to a higher diffusion potential at the junction and led to the higher V_{oc} .

observed. The shape of the curve is distinct from both a regular p-n junction or a p-i-n junction system. At zero bias, the width of the depletion region is estimated to be 0.9 μm , much smaller than the CdTe film thickness (2 μm). This suggests that the CdTe/CdS cell using ZnTe/Au as a back contact is more appropriately described as a p-n junction, albeit with a nonuniform doping concentration across the CdTe film.

As a result of our systematic investigation and optimization of the processing conditions for CdS/CdTe cell fabrication, we have made great progress in producing high efficiency cells. Table 5.6.5 lists the progress of our cell performances since we started fabricating cells in 10/92. The light I-V curve (measured at NREL) of a CdS/CdTe/ZnTe cell, which yielded a V_{oc} of 0.793 V, a J_{sc} of 20.8 mA/cm^2 , an FF of 73.18%, and an efficiency of 12.1% is shown in Figure 5.6.3. In terms of individual parameters, we have obtained V_{oc} of over 0.8 V, and FF of 74% on other cells. We also mention that an antireflection coating was not used for the cell corresponding to Fig.5.6.3. The addition of an AR coating is expected to increase the efficiency to 12.5%.

Table 5.6.5. Progress in cell performances (measured at NREL) for CdTe/CdS cells fabricated at CSM.

Date	Cell Area (cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)
01/93	0.03	0.576	16.4	0.447	4.25
06/93	0.03	0.707	21.3	0.635	9.58
12/93	0.03	0.722	21.3	0.677	10.4
11/94	0.03	0.759	22.0	0.660	11.0
03/95	0.20	0.779	21.2	0.678	11.2
04/95	0.20	0.792	20.9	0.724	12.0
04/95	0.10	0.793	20.8	0.732	12.1

Based on the light I-V measurement of an 11.2% cell, we estimated the series resistance of the cell, using the equation [9]:

$$dV/dJ = R_s + (AkT/q)(J + J_{sc})^{-1}. \quad (4)$$

By plotting dV/dJ as a function of $(J + J_{sc})^{-1}$ and extrapolating to $(J + J_{sc})^{-1} = 0$, we obtained a series resistance of 0.95 $\text{ohm}\cdot\text{cm}^2$. This value is reasonably small in comparison with those reported in the literature. The diode quality factor of the cell was obtained by plotting the diode forward current $(J + J_{sc})$ as a function of the bias across the junction $(V - JR_s)$, as shown in Fig.5.6.4. From this plot, a diode quality factor of 2.3 and a reverse saturation current density of $6 \times 10^{-8} \text{ A}/\text{cm}^2$ were obtained. The diode quality factor of greater than 2 is consistent with the values others have reported [18] and indicates that space-charge recombination is the dominant recombination mechanism.

Sample: 57BA#2
Apr 14, 1995 2:19 PM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 0.1034 cm²
Irradiance: 1000.0 Wm⁻²

$V_{oc} = 0.7931$ V
 $I_{sc} = 2.152$ mA
 $J_{sc} = 20.81$ mAcm⁻²
Fill Factor = 73.18 %

$V_{max} = 0.6616$ V
 $I_{max} = 1.888$ mA
 $P_{max} = 1.249$ mW
Efficiency = 12.1 %

after 10 min soak @ P_{max} , 1:20 cool, fast swp

Figure 5.6.3. Light I-V curve (measured at NREL) of a CdS/CdTe/ZnTe/Au cell showing 12.1% efficiency.

Figure 5.6.4. The diode forward current ($J + J_{sc}$) as a function of the bias across the junction ($V - JR_s$). The illumination intensity was 100 mW/cm^2 .

6. Summary

We have made substantial progress in understanding some of the critical issues involved in fabricating polycrystalline thin film CdTe solar cells. Primary optimization of deposition conditions of CdTe and CdS thin films has been performed. The change of CdTe and CdS film properties resulting from CdCl₂ treatment and annealing were studied.

CdCl₂ treatment and subsequent annealing induce recrystallization and grain growth in electrodeposited CdTe. By monitoring the times required for 10% recrystallization, we obtained an activation energy of 2.5 eV for the recrystallization process. We studied the annealing-induced stress in the electrodeposited CdTe. Heat treatment induces stress in CdTe films because of differences in the thermal expansion coefficients of CdTe and the substrates. For soda-lime glass substrates and the typical CdTe deposition conditions that yielded high efficiency solar cells, we observed a compressive stress in both the as-deposited and 410°C-annealed films. The magnitude of the compressive stress depends on the morphology of the CdS substrates. CdTe films deposited on CdCl₂-coated and annealed CdS substrates show higher stress than films deposited on CdS that was not coated with CdCl₂. Interdiffusion at the CdS/CdTe interface and the formation of CdTe_{1-x}S_x was also observed by monitoring the changes in XRD lineshape.

Cu-doped ZnTe was studied as a promising material for forming stable, low-resistance contacts to the p-type CdTe. The ZnTe was formed by vacuum co-evaporation of Cu and ZnTe. The electrical properties were studied systematically as a function of Cu concentration and annealing temperature. The dark resistivity of the as-deposited ZnTe decreased by more than 3 orders of magnitude as the Cu concentration was increased from 4 to 8 atomic percent. The resistivity decreased to less than 1 ohm-cm after annealing at 260°C for 30 min in vacuum. A decrease of conductivity was observed during annealing at 150 - 200°C. The activation energy of the dark conductivity of annealed ZnTe was found to be less than 50 meV.

We have investigated the effect of CdS thickness and annealing conditions on the resulting solar cells. We found that in addition to the possible changes of CdS films during annealing, the CdS film thickness may also affect the properties of the CdTe. We have explored the possibility of improving the CdS/CdTe junction properties by forming a dual-layer CdS structure. The addition of a fresh, unannealed CdS layer on annealed CdS substrates was found to enhance the V_{oc} by an average of 50 mV.

The effect of ZnTe post-deposition annealing temperature and the types of metals used to contact the ZnTe on solar cell performances were studied. Application of the ZnTe as the back contact layer to our CdTe/CdS has yielded cells with fill factors consistently exceeding 0.70 and energy conversion efficiencies consistently higher than 11%. The best cells we obtained showed a V_{oc} of 0.79 V, a J_{sc} of 20.8 mA/cm², an FF of 73.2%, and an efficiency of 12.1%. In terms of individual parameters, we have obtained a V_{oc} of over 0.8 V, and a FF of 74% on other cells.

7. Acknowledgements

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9. Appendices

9.1. Personnel

Many individuals contributed to this work. Their names, titles, and representative responsibilities are summarized below. Those who have been involved during just a portion of the project period are noted.

John U. Trefny, Professor of Physics: Project Coordinator.

Duli Mao, Research Assistant Professor: Photovoltaic Development (since 11/94).

Donghwan Kim, Research Assistant Professor: Photovoltaic Development (left CSM, 11/94).

Don L. Williamson, Professor of Physics: XRD, SAXS.

Thomas E. Furtak, Professor of Physics: Electrochemistry, Optical Properties.

Reuben Collins, Professor of Physics: Electronic and Optical Properties of Semiconductor Materials (since 10/94).

Timothy R. Ohno, Assistant Professor of Physics: Surface Physics.

Noboru Wada, Associate Professor of Physics: Raman Spectroscopy (left CSM, 06/93).

Lianghuan Feng, Visiting Professor, ZnTe Back Contact and Cell Fabrications, (since 02/94).

Dahong Du, Graduate Research Assistant: CdS Processing (deceased, 01/95; Ph.D, Applied Physics, 5/95 (posthumous)).

Andrew Johnson, Graduate Research Assistant; TCO Coatings at NREL (05/93-present).

Scott Pozder, Graduate Research Assistant: CdTe Electrochemical Processing (M.S., Materials Science, 11/94).

Bin Qi, Graduate Research Assistant: Materials Characterization (M.S., Physics, 6/94).

Yi Qu, Graduate Research Assistant: TCO Coatings (Ph.D., Materials Science, 12/93).

Jason Selby, Graduate Research Assistant: Electrodeposition of ZnTe (M.S., Materials Science, 3/95).

Yuming Zhu, Graduate Research Assistant: CdS Deposition (01/93 - present).

Nashwa Shalaan, Visiting Professor: Sample Characterization (09/92 - 11/92)

Nic Dalacu, Consultant: Electrochemical Processing (approximately 30 days total between March and September, 1992).

9.2. Laboratory Improvements

Since the inception of this project, Colorado School of Mines has spent or committed more than \$100,000 for laboratory improvements and equipment upgrades. The majority of these funds has been used to provide the processing laboratory with modern, filtered fume hoods and other hardware related to the safety of staff members and students working on the project. Plans to enlarge the facilities are currently being developed with support from the National Science Foundation.

9.3. Publications

1. "Polycrystalline CdTe Solar Cells for Large-Scale Space Applications", J.U. Trefny, Engineering, Construction, and Operation in Space III, American Society of Civil Engineers, Space '92, June 1992.
2. "Electrical and optical properties of ion beam sputtered ZnO:Al films as a function of film thickness," Qu, Y. , Gessert, T.A., Ramanathan, K., Dhere, R.G., Noufi, R., Coutts, T.J., J. Vac. Sci. & Technol. A11 996 (1993).
3. "Thin Film CdS/CdTe Solar Cells Fabricated by Electrodeposition", D. Kim, S. Pozder, B. Qi, Y. Zhu, T.E. Furtak, D.L. Williamson, and J.U. Trefny, 12th NREL Photovoltaic Program Review, AIP Conference Proceedings 306, R. Noufi and H.S. Ullal, ed. p.320, (1994).
4. "Effect of Annealing on Microstructure, Residual Stress, and Photovoltaic Characteristics of Electrodeposited CdTe Films", D. Kim, B. Qi, D.L. Williamson, and J.U. Trefny, Proc. 24th IEEE PVSC, 338 (1994).
5. "Polycrystalline Thin Film CdTe Solar Cells Fabricated by Electrodeposition", D. Kim, S. Pozder, Y. Zhu, and J.U. Trefny, Proc. 24th IEEE PVSC, 334 (1994).
6. "A study of ion-beam-sputtered ZnO films as a function of deposition temperature," Y. Qu, T.A. Gessert, T.J. Coutts, and R. Noufi, J. Vac. Sci. & Technol. A12, 1507, (1994).
7. "Electrical and optical properties of Al-doped ZnO films as a function of Al doping level," Yi Qu, T.A. Gessert, and T.J. Coutts, Thin Solid Films, to be published.
8. "Effect of Post-deposition Heat-treatment on Morphology and Microstructure of CdTe Grown by Electrodeposition", B. Qi, D. Kim, D.L. Williamson, and J.U. Trefny, J. Electrochem. Soc. (submitted).
9. "Changes of Structural and Photovoltaic Properties of Electrodeposited CdTe Thin Films During the Initial Stage of Annealing", D. Kim, B. Qi, D. Mao, D.L. Williamson, and J.U. Trefny, Solar Energy Materials and Solar Cells, (submitted).

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