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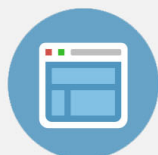
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# 13.4% efficient thin-film CdS/CdTe solar cells

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Cadmium telluride is a promising thin-film photovoltaic material as shown by the more than 10% efficient CdS/CdTe heterojunction solar cells. In this work, thin-film CdS/CdTe solar cells have been prepared using CdS films grown from an aqueous solution and *p*-CdTe films deposited by close-spaced sublimation (CSS). The properties of CdS films deposited from an ammoniacal solution of a Cd-salt, an ammonium salt, and thiourea have been controlled by optimizing the temperature and composition of the solution. The solution-grown CdS films have a high photoconductivity ratio, and its optical transmission is superior to that of vacuum evaporated CdS films. The properties of *p*-CdTe films deposited by CSS have been optimized by controlling the temperature and composition of the source material, and the substrate temperature. The properties of CdS/CdTe heterojunctions have been studied; junction photovoltage spectroscopy is used for the qualitative comparison of junction characteristics. Solar cells of 1-cm<sup>2</sup> area with an AM 1.5 efficiency of 13.4% are reported.

## I. INTRODUCTION

Cadmium telluride (CdTe), a direct gap semiconductor with a room-temperature band-gap energy of 1.5 eV, is a promising thin-film photovoltaic material. Because of the short optical absorption length in CdTe and the difficulty of forming a thin-film shallow junction with a high conductivity surface layer, thin-film CdTe solar cells are of the heterojunction configuration. A transparent conducting semiconductor (TCS) is used as the heterojunction partner. Essentially all known TCSs, nonstoichiometric or doped oxides and sulfides, such as cadmium sulfide (CdS), tin oxide (SnO<sub>2</sub>), and zinc oxide (ZnO), are *n* type. *p*-CdTe films are therefore used as the absorber. CdS has been found to be best suited for thin-film CdTe heterojunction solar cells, and conversion efficiencies of higher than 10% have been reported for CdS/CdTe solar cells prepared by several techniques.<sup>1-8</sup> In efficient solar cells, CdS films are deposited by spray pyrolysis, vacuum evaporation, or close-spaced sublimation, and CdTe films are deposited by close-spaced sublimation, electrodeposition, spraying, or screen printing. However, the potential of thin-film CdTe solar cells has not been fully realized, and further work is underway at many organizations worldwide.

In this work, efficient thin-film CdS/CdTe heterojunction solar cells have been prepared from CdS deposited from an aqueous solution, a low-temperature and low-cost technique, and CdTe deposited by close-spaced sublimation, also a cost-effective, easily scalable technique. The solar cell is of the back-wall configuration, i.e., films of CdS, *p*-CdTe, and an ohmic contact are deposited successively onto a fluorine-doped tin oxide-coated glass (SnO<sub>2</sub>:F/glass) substrate. SnO<sub>2</sub>:F, with a sheet resistance of about 10 Ω per square, obtained through the courtesy of Watkin-Johnson, is used to reduce the sheet resistance of CdS. The deposition and properties of CdS and *p*-CdTe films and the characterization of CdS/CdTe solar cells are summarized in this paper.

## A. Cadmium sulfide films

Cadmium sulfide (CdS) is a commonly used TCS for optoelectronic devices. Several techniques including vacuum evaporation, chemical vapor deposition, electrodeposition, spray pyrolysis, precipitation from aqueous solutions, etc. have been used for the deposition of CdS films. The deposition of CdS films from an aqueous solution is perhaps the most cost effective, easily controlled process for solar cells. The solution growth process is based on the reaction of a cadmium salt, a complex agent, and a sulfur compound in a heated aqueous solution. A variety of source materials has been used:<sup>9-13</sup> (1) the acetate, chloride, nitrate, or sulfate as the cadmium source, (2) ammonium hydroxide, potassium cyanide, or triethanolamine as the complexing agent, and (3) thiourea or thioacetamide as the sulfidizing agent. However, information on the use of solution-grown CdS for photovoltaic devices is very limited. For example, Cu<sub>2</sub>S/CdS solar cells made by dipping CdS films on metal substrates in a cuprous chloride solution has been found to have poor photovoltaic characteristics ( $V_{oc}$  of 200 mV,  $J_{sc}$  of 2.7 mA/cm<sup>2</sup>, and 0.13% efficiency under 1 sun illumination).<sup>10</sup> As a comparison, Cu<sub>2</sub>S/CdS solar cells prepared from sprayed CdS films have conversion efficiencies of 5-7%,<sup>14</sup> and those from evaporated CdS films have conversion efficiencies in excess of 9%.<sup>15</sup>

Thin films of CdS have been deposited on glass and SnO<sub>2</sub>F/glass substrates from an aqueous solution of 50-90 °C containing a Cd-salt (acetate, chloride, or nitrate), an ammonium salt (acetate, chloride, or nitrate), ammonium hydroxide, and thiourea at concentrations in the ranges of  $(5-100) \times 10^{-4}$  M,  $(2.5-100) \times 10^{-3}$  M, 0.05-1 M, and  $(5-100) \times 10^{-4}$  M, respectively. The formation of CdS may take place heterogeneously on the substrate surface and homogeneously in solution. The homogeneous process should be minimized since the CdS particulates formed in solution can be adsorbed on the growing surface yielding films of uncontrolled properties. The heteroge-

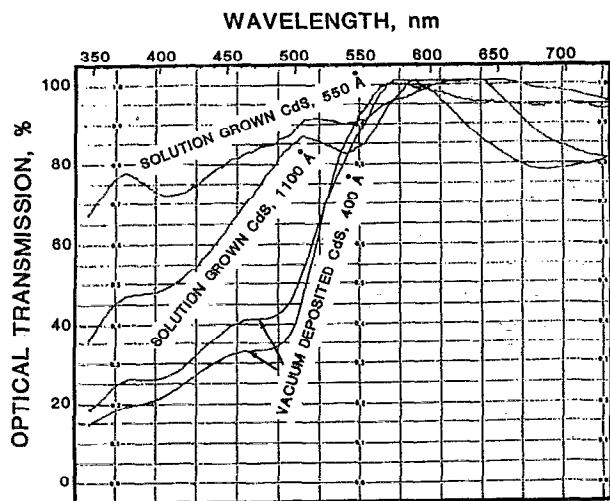


FIG. 1. Optical transmission spectra of CdS films deposited by solution growth and by vacuum evaporation.

neous process is promoted at lower reaction rates. The reaction rates can be controlled by the temperature and the pH of the solution, the concentration of the Cd-salt, the thiourea/Cd-salt molar ratio, and the  $\text{NH}_4$ -salt/Cd-salt molar ratio. Adherent CdS films have been deposited under a wide range of conditions at average rates of 25–50 Å/min. Films deposited on  $\text{SnO}_2\cdot\text{F}$ -coated glass are more adherent than those on glass substrate. Further, CdS films of 500 Å or less in thickness deposited on glass substrates over a wide range of deposition conditions are often discontinuous. This is due to the difficulty of the nucleation of CdS on the smooth surface of an amorphous substrate. Once the nuclei are formed, further deposition tends to continue the growth of existing nuclei rather than initiating nucleation. The nucleation of CdS on  $\text{SnO}_2\cdot\text{F}$ /glass takes place more readily, resulting in continuous films at small thicknesses.

CdS films deposited with minimal homogeneous reaction are highly adherent with smooth and reflective surfaces. The films are polycrystalline, consisting of crystallites of several hundred angstroms in dimensions. X-ray diffraction indicates that the films show a preferred (0001) orientation. The optical absorption of CdS films was measured using a Varian Model Cary 17D spectrophotometer. The films deposited from solutions of various compositions showed essentially the same absorption characteristics. Figure 1 shows the transmission spectra of two solution-grown CdS films of 550 and 1100 Å thickness, where the change in optical transmission is gradual because of the small film thickness. The transmission characteristics of two CdS films deposited by vacuum evaporation are also shown in Fig. 1 for comparison. The vacuum evaporated films show relatively low transmission in the above-gap region due presumably to nonstoichiometry associated with S vacancies. The difference in optical transmissions of two vacuum deposited CdS films of similar thickness may be related to different degrees of nonstoichiometry in the films. The high optical transmission of solu-

tion-grown films suggests that these films are essentially stoichiometric. The optical band gap of solution grown CdS films of 1500–2000 Å thickness, deduced from the square of the absorption coefficient versus photon energy plot in the usual manner, is 2.42–2.43 eV.

The lateral electrical resistivity of CdS films on glass substrates was measured at room temperature using a planar configuration. Four collinear contacts were made to the films by using a Ga-In alloy. The current is passed through the outer contacts, and the potential drop measured across the two inner contacts. The resistivity was also measured under illumination with ELH lamps at 100  $\text{mW}/\text{cm}^2$ . The room-temperature dark resistivity is  $10^5$ – $10^6$  Ω cm, and the illuminated resistivity is 50–300 Ω cm. The dark resistivity of solution-grown CdS films is considerably lower than the intrinsic resistivity, due presumably to adsorbed moisture, contaminations, etc. Since a thin film (500–1000 Å) of CdS is used for solar cells and the solar cell operates under illumination, the as-grown CdS film is well suited as the TCS for CdTe solar cells.

## B. Cadmium telluride films

Polycrystalline CdTe films have been deposited by several techniques including electrodeposition,<sup>4</sup> close-spaced sublimation (CSS),<sup>1–3</sup> reaction between cadmium, cadmium iodide, and tellurium under reduced pressure,<sup>16</sup> and direct combination of elemental cadmium and tellurium.<sup>17</sup> Each technique has its own merits. For example, the combination of elemental vapors is most flexible, the electrodeposition in aqueous solutions is most energy efficient, and the CSS technique produces CdTe films at high rates. The CSS technique is used in this work.

The deposition of CdTe films by the CSS technique is based on the reversible dissociation of CdTe at high temperatures:



A CdTe source and a substrate are separated by a small distance in a controlled atmosphere, and the source is maintained at a higher temperature than the substrate. The source CdTe dissociates into its elements (CdTe does not exist in the vapor phase) which recombine on the substrate surface, depositing CdTe films. This process provides direct transport of each component of the source across the space to the substrate, and in most cases, the rate of the transport is diffusion-limited. Since the dissociation pressure of CdTe increases exponentially with increasing temperature, the deposition rate of CdTe films should show a similar dependence on the temperature of the source material. At a given temperature of the source material, the deposition rate of CdTe films should increase rapidly with increasing pressure in the reaction chamber.

The apparatus used for the deposition of CdTe films by the CSS technique is shown schematically in Fig. 2.<sup>3</sup> Briefly, Corning 7059 glass,  $\text{SnO}_2\cdot\text{F}$ /glass or CdS/ $\text{SnO}_2\cdot\text{F}$ /glass were used as substrates. Polycrystalline CdTe synthesized by the direct combination of the elements and a dopant (such as arsenic or antimony) or commercially available

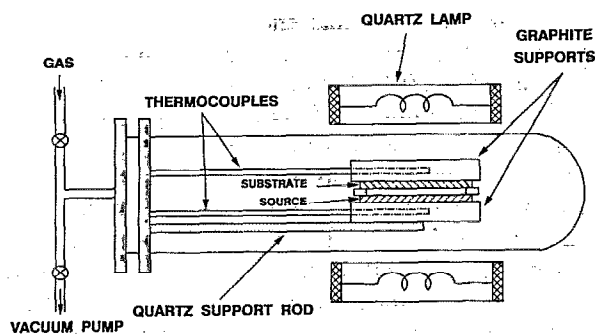


FIG. 2. Schematic diagram of the apparatus for the deposition of CdTe films by the CSS technique.

polycrystalline CdTe of 99.999% purity was used as the source material. The substrate and the source material were supported by appropriate holders and enclosed in a controlled atmosphere in a fused silica tube provided with gas inlet and outlet tubes. They were maintained at desired temperatures by using quartz lamps, and thermocouples inserted into the holders were used to control their temperatures (due to the location of the thermocouples, the true temperature of the source is lower than the temperature indicated by the thermocouple, and that of the substrate is higher than the temperature indicated by the thermocouple). The important parameters of the CSS technique are: the temperatures of the source and the substrate, the separation between the source and the substrate, the pressure in the reaction tube, and the composition of the source material. In most deposition experiments, the substrate at 580–620 °C was separated from the CdTe source material by 0.1–0.2 cm in a reaction chamber of 30–300 Torr, and the source-substrate temperature difference was 80–120 °C. The deposition rate can be controlled between 1 and 10  $\mu\text{m}/\text{min}$  by varying the source and substrate temperature and the pressure in the reaction chamber.

The microstructure of CdTe films depends on the crystallinity of the substrate, the substrate temperature, and the rate of deposition. In general, the grain size increases with increasing substrate temperature and increasing film thickness, and the grains become more closely packed at low deposition rates. The nucleation of CdTe on glass substrates is more difficult than that on CdS- or  $\text{SnO}_2$ -coated glass substrates. Thus, the CdTe film deposited on glass substrates consists of crystallites with well developed faces and is usually not continuous, while that on CdS substrates consists of closely packed crystallites. This is illustrated in Fig. 3, where the scanning electron micrographs of CdTe films of about 10  $\mu\text{m}$  thickness deposited on glass and CdS/ $\text{SnO}_2$ :F/glass substrates at 600 °C are shown. Further, x-ray diffraction data indicate that the CdTe film on glass substrates is essentially polycrystalline and that the CdTe film on CdS/ $\text{SnO}_2$ :F/glass substrates shows a strong preferred (111) orientation.

Two major problems associated with the fabrication of thin-film CdTe solar cells are the difficulty of producing

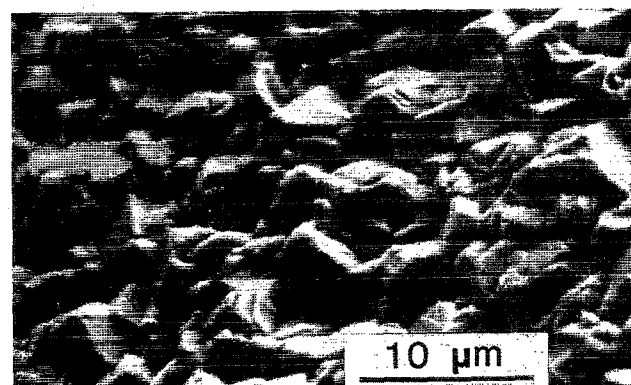
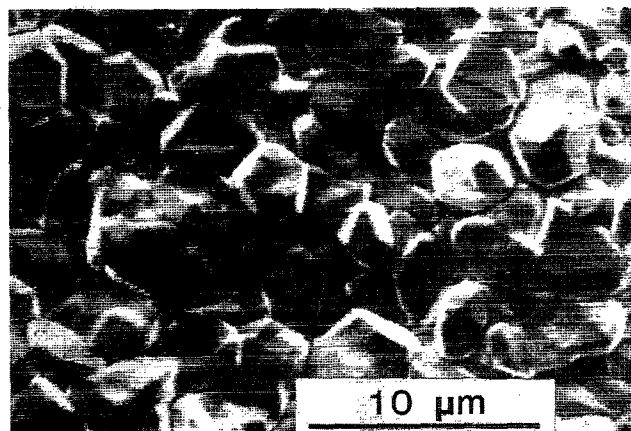


FIG. 3. Scanning electron micrographs of CdTe films deposited on glass (upper) and CdS/ $\text{SnO}_2$ :F/glass (lower) substrate.

low-resistivity  $p$ -CdTe films, and the difficulty of forming stable low resistance contacts to the  $p$ -CdTe films. The lateral resistivity may be measured by the potential probe method using CdTe films deposited on glass substrates. Low resistance contact is not necessary for this measurement; however, the lateral resistivity of CdTe films is usually very high,  $10^5 \Omega \text{ cm}$  or greater, due to the potential barrier at grain boundaries. The resistivity of CdTe films in the thickness direction is more related to the device function, and this measurement requires reproducible, stable, low-resistance contact to  $p$ -CdTe films. The formation of low resistance contact to  $p$ -CdTe is difficult because of its large work function, 5.5 eV or higher depending on the carrier concentration. Two common approaches to the contact formation are: (1) the use of contact materials with a higher work function than  $p$ -CdTe, and (2) the formation of a  $p^+$ -region under the contact by the reaction or in-diffusion of the contact material to reduce the barrier height. In the first approach, low-resistivity HgTe, deposited by the combination of elemental vapors,<sup>18</sup> and  $p^+$ -ZnTe, deposited by vacuum evaporation of Cu-doped ZnTe,<sup>19</sup> have been shown to be satisfactory contact materials. In the second approach, graphite pastes doped with Au, Cu, and Hg salts<sup>20</sup> have been found to be suitable since interlayers of  $\text{Au}_2\text{Te}$ ,  $\text{Cu}_2\text{Te}$ , and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  of high

carrier concentrations are readily formed. The surface preparation of *p*-CdTe appears to be important, etching with a  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4 + \text{HNO}_3$  solution is usually used to provide a Te-rich surface.<sup>2</sup> Low-resistivity (5–10  $\Omega \text{ cm}$ ) As-doped ZnTe films deposited from dimethylzinc and diisopropyltellurium<sup>21</sup> and doped graphite paste have been used as ohmic contact to *p*-CdTe films. In addition, a  $\text{AuCl}_3$  is readily reduced by CdTe to form a Au/CdTe contact; however, this contact has a life of 1–2 days due to the high diffusivity of Au.

Since the *p*-CdTe/CdS or the *p*-CdTe/ $\text{SnO}_2$  interface is rectifying, the electrical resistivity of CdTe films in the thickness direction can be deduced from the forward dark current-voltage characterization of contact/CdTe/CdS/ $\text{SnO}_2$ :F/glass or contact/CdTe/ $\text{SnO}_2$ :F/glass structures. At low voltages, the carrier recombination in the space-charge region and the carrier injection across the junction determine the current flow. The series resistance dominates at higher voltages, on the order of 1.5 V. If one assumes that the contact/*p*-CdTe interface resistance is small compared with the contribution of the resistance of CdTe, then the upper limit of the resistivity can be deduced from the series resistance. The series resistance of device structures with CdTe films of 5–10  $\mu\text{m}$  thickness has been measured to be in the range of 0.5–1  $\Omega \text{ cm}^2$ , corresponding to a CdTe resistivity of 500–2000  $\Omega \text{ cm}$ .

### C. CdS/CdTe heterojunction solar cells

Thin-film CdS/CdTe heterojunctions have been prepared by depositing 3–5  $\mu\text{m}$  of *p*-CdTe films on CdS films of 500–1500  $\text{\AA}$  thickness grown on  $\text{SnO}_2$ :F/glass substrates. Junction photovoltage (JPV) spectroscopy is a convenient technique for the qualitative evaluation of the heterojunction structure, since this type of open-circuit measurement does not require a low-resistance contact to *p*-CdTe. A graphite paste was applied to the surface of *p*-CdTe, and the JPV spectrum was measured in the wave-

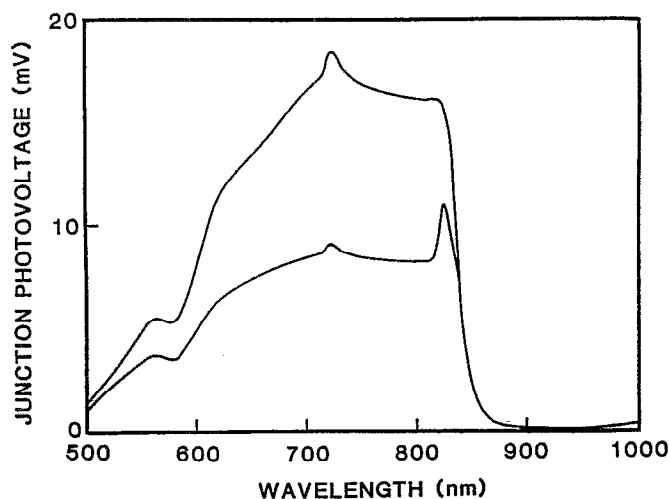


FIG. 4. Junction photovoltage spectra of two *p*-CdTe/CdS/ $\text{SnO}_2$ :F/glass structures showing the difference in carrier collection.

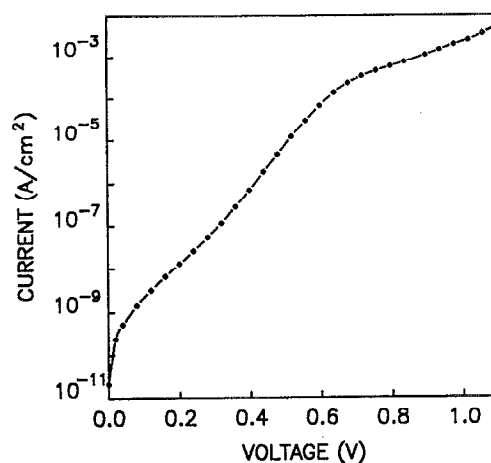


FIG. 5. Dark current-voltage characteristics of a thin-film CdS/CdTe heterojunction solar cell.

length range of 500–1000 nm by illuminating the glass surface with a 105-W tungsten-halogen (FCS) lamp. This light source shows approximately linear increase in intensity wavelength in the spectral range under study. Figure 4 shows JPV spectra of two *p*-CdTe/CdS/ $\text{SnO}_2$ :F/glass structures showing widely different carrier-collection behavior. At photon energies above the band-gap energy, the absorption coefficient of CdTe increases with increasing photon energy. The short wavelength radiation is absorbed in CdTe near the CdS/CdTe interface. As the wavelength of the incident radiation is increased, the absorption takes place predominantly away from the interface. All carriers generated within the depletion region are collected to produce a photovoltage. The photoresponse cut-off wavelength corresponds to the band-gap energy of CdTe. The integrated area under the JPV spectrum is the open-circuit voltage of the heterojunction under illumination with the 150-W tungsten-halogen lamp. Thus, the magnitude of the

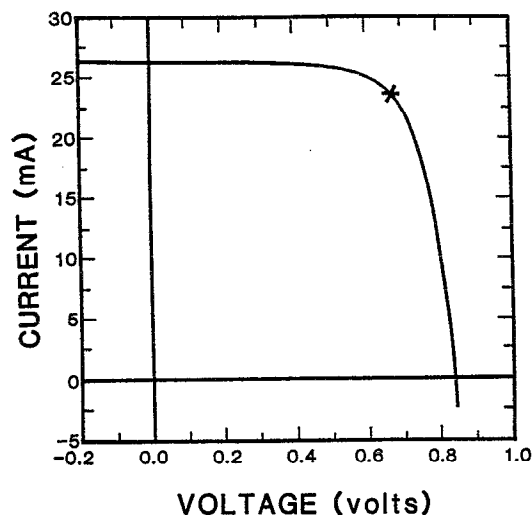


FIG. 6. Current-voltage characteristics of a thin-film CdS/CdTe solar cell of 1.2-cm<sup>2</sup> area under global AM 1.5 conditions.

photovoltage signal and the spectral distribution of the photoresponse are useful criteria for the comparison of CdTe/CdS heterojunctions.

The typical dark current-voltage characteristics of a CdS/CdTe heterojunction solar cell at forward bias of up to 1 V is shown in Fig. 5. At higher voltages, 1.5 V and above, the current-voltage characteristics become linear due to the predominance of series resistance. Using the relation  $J=J_0 [\exp (qV/nkT) - 1]$ , the diode quality factor and saturation current density deduced from the semilog plot are  $1.65$  and  $6 \times 10^{-11}$  A/cm<sup>2</sup>, respectively. Figure 6 shows the current-voltage characteristics of a solar cell of  $1.2\text{-cm}^2$  area under global 1.5 illumination, measured at the Solar Energy Research Institute. The open-circuit voltage, short-circuit current density, and fill factor, are  $0.84$  V,  $21.9$  mA/cm<sup>2</sup>, and  $72.6\%$  respectively, corresponding to a conversion efficiency of  $13.4\%$ . This is believed to be the highest efficiency reported for a  $1\text{-cm}^2$  area thin-film solar cell. One expects that the short-circuit current density can be increased appreciably and that a  $15\%$  conversion efficiency can be achieved.

## ACKNOWLEDGMENT

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