Thin-film CdS/CdTe solar cell with 15.8% efficiency

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This letter describes the fabrication and characteristics of high-efficiency thin-film CdS/CdTe heterojunction solar cells. CdS films have been prepared by chemical bath deposition and *p*-CdTe films have been deposited by close-spaced sublimation. A CdS/CdTe solar cell of greater than 1 cm^2 area with an AM1.5 efficiency of 15.8% is reported.

Among the candidates for thin-film solar cells capable of a significant conversion efficiency of light into electricity, CdTe has shown considerable promise. CdTe has the advantage of a nearly ideal band gap for solar terrestrial photoconversion (1.45 eV) and a short absorption length when compared to grain sizes typically encountered. This latter property reduces recombination at grain boundaries, a major problem with other polycrystalline materials. As a result, a large fraction of the photogenerated carriers are generated within the depletion layer allowing more efficient collection.

Because it is difficult to produce thin-film CdTe solar cells with thin *n*-CdTe layers, heterojunctions utilizing wide-band-gap *n*-type semiconductors and *p*-CdTe are most common. CdS has a band gap of 2.42 eV and is the most commonly employed heterojunction partner to *p*-CdTe due to its similar chemical properties. Control of the CdS/CdTe interfacial chemistry is critical to achieving high solar conversion efficiencies.[1] Compounding this difficulty is the necessity to use a small thickness of CdS for enhanced short-wavelength response.

A wide variety of techniques are available for depositing thin films of CdTe. The close-spaced sublimation (CSS) process offers the advantages of uncomplicated deposition apparatus and a high transport efficiency conducted under low vacuum conditions at moderate temperatures, thus simplifying scale-up for high volume continuous processing. Although techniques such as electrodeposition[2] and spraying[3] have produced CdS/CdTe devices with efficiencies greater than 12%, to this date close-spaced sublimation has demonstrated the highest conversion efficiency of 14.6%.[4] This letter reports a thin-film CdS/CdTe solar cell with a total area conversion efficiency of 15.8% under AM1.5 illumination.

CdTe/CdS solar cells were fabricated in the superstrate configuration shown in Fig. 1. SnO_2 was used to provide a low resistance contact to CdS. SnO_2 films were deposited by MOCVD on Corning 7059 glass in a rf heated system from the reaction between tetramethyltin and oxygen. The SnO_2 films were doped with fluorine by introducing $CFBr_3$, a commercially available Freon, into the reaction mixture. Typical flow rates were 20 cc/min TMSn, 500 cc/min O_2, and the substrate temperature was maintained at a temperature between 425 and 500 °C. The sheet resistance of the SnO_2:F films was typically 7–10 Ω/□ and the sub-band-gap transmission was greater than 90% over much of the visible spectrum.

Thin films of CdS were formed on the SnO_2:F/glass structures by chemical bath deposition (CBD). The CBD process is a simple technique to deposit thin, adherent, and optically transparent CdS films. CdS is formed from the reaction between cadmium acetate and thiourea in an ammoniacal solution. CBD CdS films were deposited with a typical thickness 0.07–0.10 μm, allowing a significant portion of supraband-gap (>2.42 eV) radiation to be transmitted to the *p*-CdTe layer. The heterogeneous formation of CdS was promoted by slow deposition rates (20 Å/min). The deposition rate was regulated by the addition of a buffer, ammonium acetate, to the bath. The concentrations of cadmium acetate, ammonium acetate, thiourea, and ammonium hydroxide were typically $(1–5)\times10^{-4}$, $(1–3)\times10^{-2}$, $(1–5)\times10^{-3}$, and 0.1–0.5 M, respectively, and the bath temperature was maintained at 90 °C.

After the deposition of CdS, the substrates were cleaned ultrasonically, rinsed with deionized water, and blown dry with nitrogen. A substrate was then loaded into the CSS deposition chamber. Prior to the deposition of CdTe, and the CdS/SnO_2:F/glass structure was annealed for 5–20 min in a hydrogen atmosphere at a temperature between 350 and 425 °C. This treatment has been found helpful in achieving large fill factors in the finished devices.

The source material for the CSS deposition was CdTe of 99.999% purity. The substrate and source material were mounted 0.2 cm apart against graphite blocks supported inside a quartz reaction vessel. External quartz lamps heated the graphite blocks radiatively and thermocouples were used to monitor their interior temperatures. Typical source and substrate temperatures were 600° and 700 °C, respectively. Under these conditions the sublimation is limited by diffusion and the growth rate is determined by the pressure and ambient. At these temperatures, the growth

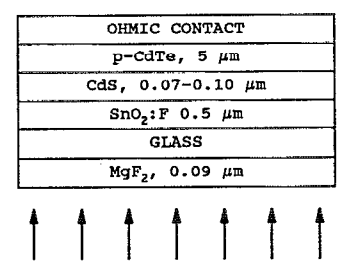

FIG. 1. Configuration of a thin-film CdTe solar cell.

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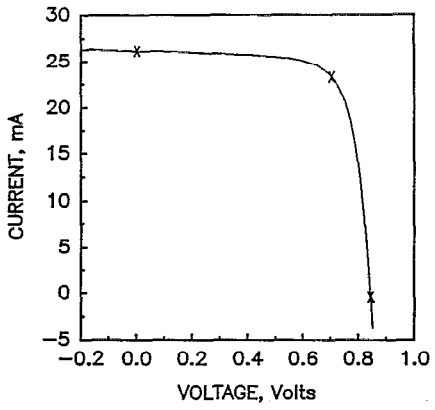

FIG. 2. Current-voltage characteristics of a thin-film CdS/CdTe solar cell under global AM1.5 conditions. Area=1.05 cm^2, V_{oc}=0.8429 V, J_{sc}=25.09 mA/cm^2, fill factor=74.48%, and efficiency=15.8%.

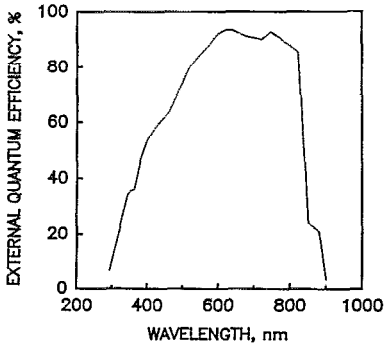

FIG. 3. The quantum efficiency of the thin-film CdS/CdTe solar cell shown in Fig. 2.

rate in a controlled atmosphere at 30 Torr was about 1 μm/min. Typically, a 5μm CdTe film was deposited by CSS onto the annealed CdS/SnO_2:F/glass structure.

The CdTe films deposited under these conditions are polycrystalline and adherent to the substrate. The as-deposited films are *p*-type with a typical grain size of 3–5 μm. After cooling, the coated substrate was removed from the deposition chamber and subjected to a commonly used post-deposition heat treatment.[5,6] The carrier concentration of CdTe films, determined from capacitance-voltage measurements of CdS/CdTe junctions, is 8×10^{14}–2×10^{15} cm^{-3} as-deposited, and $(1–3)\times10^{14}$ cm^{-3} after the post-deposition heat treatment.

Ohmic contact to CdTe has traditionally been a difficult task because of the large work function of CdTe. A buffer layer of high conductivity *p*-type semiconductor, such as *p*-ZnTe or *p*-HgCdTe, on the surface of the CdTe is a commonly used solution to this problem.[7] Application of a graphite paste containing a Hg compound followed by a low-temperature (250–275 °C) anneal was found to function as an adequate electrical contact in this work. To form the contacts, areas of about 1 cm^2 area on the CdTe surface were masked, the contact material was applied, and the structure was annealed in an inert atmosphere. After cooling, the cells were isolated by scribing. In solder was applied to SnO_2 to form a rugged contact. In some cases a MgF_2 antireflection coating was applied to the front glass surface. The thickness of the AR coating was optimized for maximum transmission at 500 nm.

Current-voltage measurements of the CdS/CdTe heterojunctions were performed in the dark and under AM1.5 illumination. Junction parameters were extracted by fitting a single-diode model to the device characteristics. In the dark condition, the saturation current density was typically $(2–5)\times10^{-12}$ A/cm^2, and the diode quality factor varied in the range 1.6–1.9. Under illumination, the diode quality factor was typically 2.0–2.5, shunt resistance 1–3 kΩ cm^2, and series resistance less than 0.8 Ω cm^2. The illuminated characteristics of several devices were measured at the National Renewable Energy Laboratory (NREL) under global AM1.5 conditions. The characteristics of one solar cell are shown in Fig. 2, where the open-circuit voltage, short-circuit current density, and fill factor are 843 mV, 25.1 mA/cm^2, and 74.5%, respectively, corresponding to a total area conversion efficiency of 15.8%. The quantum efficiency of this device is shown in Fig. 3. The reduced response at shorter wavelengths indicates the primary loss in this cell is window layer absorption. The 15.8% conversion efficiency is believed to be the highest ever reported for a thin-film solar cell.

The high temperatures used during the deposition of CdTe by CSS may cause the formation of an interdiffused region between CdS and CdTe. The presence of a $Cd_xS_{1-x}Te$ region would shift the electrical junction away from the metallurgical junction and improve the electrical and photovoltaic characteristics. The degree of diffusion is controlled by the substrate temperature and the deposition rate. Further work to investigate the effects of these process parameters on CdS/CdTe thin-film solar cells is underway.

[1] I. Clemminck, M. Burgelman, M. Casteleyn, J. De.Poorter, and A. Vervaet, *Proceedings of the 22nd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1991), p. 1114.
[2] J. M. Woodcock, A. K. Turner, M. E. Ozsan, and J. G. Summers, *Proceedings of the 22nd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1991), p. 842.
[3] R. K. Ahrenkiel, B. M. Keyes, L. Wang, and S. P. Albright, *Proceedings of the 22nd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1991), p. 940.
[4] T. L. Chu, S. S. Chu, J. Britt, C. Ferekides, C. Wang, C. Q. Wu, and H. S. Ullal, IEEE Electron Device Lett. **13**, 303 (1992).
[5] S. A. Ringel, A. W. Smith, M. H. Macdougal, and A. Rohatgi, J. Appl. Phys. **70**, 881 (1991).
[6] S. S. Ou, O. M. Statsudd, and B. M. Basol, J. Appl. Phys. **55**, 3769 (1984).
[7] B. M. Basol and E. S. Teng, Appl. Phys. Lett. **48**, 946 (1986).