

All-sputtered 14% CdS/CdTe thin-film solar cell with ZnO:Al transparent conducting oxide

Akhlesh Gupta^{a)} and Alvin D. Compaan

Department of Physics and Astronomy, University of Toledo, Toledo, Ohio, 43606

(Received 16 February 2004; accepted 27 May 2004)

Radio-frequency (rf)-sputtered Al-doped ZnO was used as the transparent front contact in the fabrication of high efficiency superstrate configuration CdS/CdTe thin-film solar cells. These cells had CdS and CdTe layers also deposited by rf sputtering at 250 °C with the highest processing temperature of 387 °C reached during a post-deposition treatment. The devices were tested at National Renewable Energy Laboratory and yielded an efficiency of 14.0%, which is excellent for a CdTe cell using ZnO and also for any sputtered CdTe solar cell. The low-temperature deposition process using sputtering for all semiconductor layers facilitates the use of ZnO and conveys significant advantages for the fabrication of more complex multiple layers needed for the fabrication of tandem polycrystalline solar cells and for cells on polymer materials. © 2004 American Institute of Physics. [DOI: 10.1063/1.1775289]

Solar cells generally require a high conductivity transparent front contact layer to facilitate current collection. In most cells, this front contact is deposited last and therefore does not need to survive further processing except usually for a contact grid. However, CdTe cells operate best in a “superstrate” configuration in which the light enters the active junction through the glass. In this case, the transparent “front” contact is deposited first and must survive all subsequent deposition steps and any postdeposition processing. The best CdTe cells to date typically have used processing at 550–650 °C. Fluorine-doped tin oxide (SnO₂:F) is one of the few materials robust enough for these devices and has been used to produce CdTe cells with 15.8% efficiency.¹ Recently stannate materials (Cd₂SnO₄ and Zn₂SnO₄) have been used to achieve 16.5% efficient CdTe cells,² although this also requires processing above 600 °C.

Doped ZnO, especially Al-doped ZnO (ZnO:Al), shows excellent transparency over the entire visible spectrum and has better transport properties than SnO₂:F due to higher electron mobility. Although ZnO:Al is used as the final layer in substrate configuration copper–indium–gallium–diselenide cells, attempts to utilize it as the transparent conducting oxide (TCO) in superstrate configuration solar cells, such as CdTe, have not been very successful.^{3–5} This results from its thermal instability and reaction with CdS (Ref. 5) at the high growth temperature needed, e.g., by close-spaced-sublimation,⁴ and vapor-transport-deposition techniques and its instability in high acidic or basic media used, e.g., during solution growth or electrodeposition techniques.⁶ The best efficiency reported for a CdS/CdTe cell on a ZnO:Al TCO is ~9%.³

Although CdTe thin-film solar cells have been prepared by several techniques, a low-temperature deposition technique, such as magnetron sputtering⁷ provides the opportunity to explore the use of ZnO:Al as a front contact in the superstrate configuration CdS/CdTe solar cell. Here, we provide comparisons between the characteristics of the ZnO:Al and SnO₂:F and describe the advantages of ZnO:Al as a TCO in an all-sputtered device.

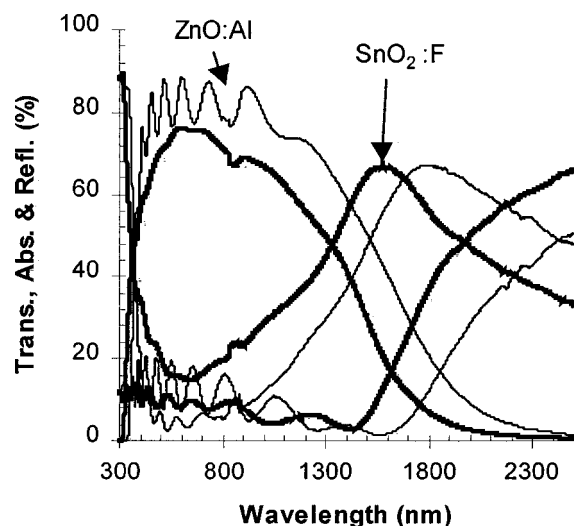
The ZnO:Al films were deposited using unbalanced-magnetic-field, planar-rf-magnetron sputtering from a ceramic ZnO:Al₂O₃ (2%) target at 220 °C on 1 mm thick aluminosilicate (ASG) or sodalime glass (SLG) slides. The depositions were carried out in pure argon at 48 W of rf power from a 50 mm diameter target, at 10 to 12 mTorr pressure and a deposition rate of ~2 Å/s. The target–substrate distance was 70 mm. The thicknesses of the as-deposited ZnO:Al films were calculated from optical interference fringes⁸ and measured with a stylus profilometer. In this geometry, a 30% drop in thickness occurs between the center and the edge of the 6 cm×6 cm deposition area.

Sputtered ZnO is known to be sensitive to neutral and charged species bombardment damage,⁹ and therefore, the optical and electrical properties of center and edge were different. A comparison of optical properties between the center and edge areas (not shown) indicated that, although both areas show similar transparency in the visible, the edge area transmits to a longer wavelength at half intensity (1350 versus 1200 nm) and the plasma reflectivity edge (half intensity reflectivity) moves to a shorter wavelength (1670 versus 1780 nm). These indicate higher intragrain mobility and higher carrier concentration in the edge area.

Routinely, we have used SnO₂:F (~0.5 μm) on 3 mm (SLG) for our standard fabrication of CdS/CdTe cells. This TCO (TEC-7), a commercial product of Pilkington, plc,¹⁰ incorporates a diffusion barrier/color suppression layer and has some haze [surface root-mean-square (rms) roughness of ~37 Å]. Figure 1 shows a comparison of the optical properties of a TEC-7 substrate and our sputtered ZnO:Al (~0.7 μm) on a 1 mm thick SLG microscope slide. All plots are for the film on a substrate with no substrate in the reference beam. The TEC-7 glass shows more absorbance and ~12% less transmittance over the visible region. The optical properties of TCOs in the near-infrared (near-IR) part of the spectrum can be used to estimate the free carrier concentration.¹¹ Both absorbance and reflectance plots show a lower plasma wavelength for SnO₂:F due to higher carrier concentration.

Commercial TCOs generally have a SiO_x barrier layer between the SLG substrate and the TCO (Ref. 12) to prevent

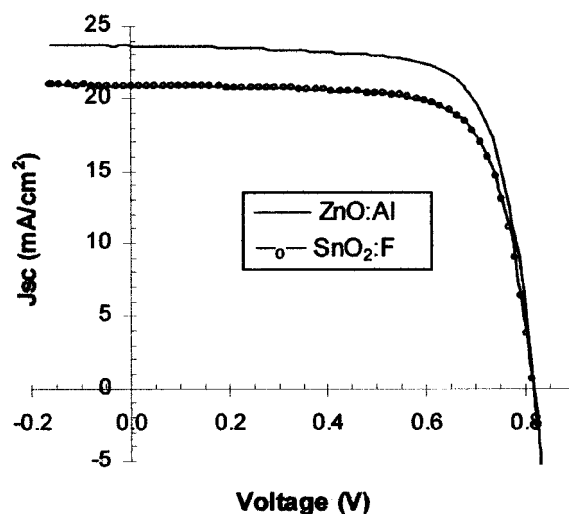
^{a)}Electronic mail: agupta@physics.utoledo.edu

FIG. 1. Comparison of the optical properties of ZnO:Al and SnO₂:F.

the diffusion of sodium from the SLG into the TCO during processing. Since we do not have the capability to deposit such a barrier layer, we used ASG as the substrate. To determine whether the properties of the sputtered ZnO:Al are sensitive to the substrate, we compared ZnO:Al deposited on ASG with that deposited on SLG, both 1 mm thick, in the same deposition run. The ZnO:Al film on the SLG substrate is slightly more transparent in the near IR, consistent with some loss of carrier concentration when deposited on the SLG substrate.

Hall measurements on the ZnO:Al/ASG and SnO₂:F/SLG structures are presented in Table I. While the optical measurements showed differences in transmission and absorption between the center and the edges of the ZnO:Al films, the Hall measurement showed almost the same mobility and carrier concentration. The difference in results from the two measurement techniques could be due to the fact that Hall technique measures bulk in-plane transport properties, in which the effect of grain boundaries may dominate. Optical measurements, by contrast, measure microscopic bulk properties in which grain-boundary scattering is of secondary importance. The measured mobility is higher and the carrier density is lower for ZnO:Al than for SnO₂:F in agreement with the optical measurements. The resistivity is almost the same for both TCOs, but the thicker ZnO:Al has a lower sheet resistance. Furthermore, the factor of 2 higher mobility of ZnO:Al measured in Hall transport and the correspondingly narrower absorbance peak, provides advantages for photovoltaic applications.

The higher optical transparency is clearly important, but also the lower sheet resistance would allow the design of monolithically interconnected solar modules with increased

FIG. 2. Comparison of current-voltage curves of CdS/CdTe solar cells on ZnO:Al and SnO₂:F.

cell width, fewer interconnect junctions, and hence decreased dead area due to scribing. This would increase the power per unit area of the modules. We have included for comparison in Table I the electrical characteristics of one of the best ZnO:Al films reported in literature.¹³ The carrier concentration of our films is lower by a factor of 3 but the mobility of our ZnO:Al is higher by ~20%, probably due to less ionized impurity scattering. Our cell results given below illustrate these advantages.

The most important aspect of this work is the demonstration that the sputtered ZnO:Al can be used in superstrate structure CdS/CdTe solar cells. We have made a comparison of the two types of TCO for sputtered cells. Devices were fabricated on as-deposited ZnO:Al/ASG (1 mm) or commercial SnO₂:F/SLG (3 mm) by deposition of 130 nm thick CdS and 2.3 micron CdTe layers using rf-magnetron sputtering at 250 °C as described earlier.⁷ The deposited structures received the usual vapor CdCl₂ treatment at 387 °C in dry air followed by an evaporated Cu/Au back contact.⁷

Figure 2 shows the comparative current-voltage curve and Table II gives summaries of the cell performance data obtained at National Renewable Energy Laboratory using an air-mass 1.5 spectrum. The comparison shows that the major difference between the two types of cells is the higher current achieved with the ZnO:Al/ASG substrates. While the open-circuit voltage, V_{OC} , and the fill factor, FF, are almost same for the two devices, the ZnO:Al-based device showed an improvement in the short-circuit current, J_{SC} , by 15%. The effect of lower sheet resistance of ZnO:Al TCO is also clearly visible by the lower series resistance of the cell. The efficiency of the device increased from 12.6% to 14.0% entirely due to increased J_{SC} because of higher transmission of the glass/ZnO:Al in visible region. This is the highest effi-

TABLE I. Hall measurement data for ZnO:Al and SnO₂:F.

Sample ID	t (μm)	Sheet resistance (Ω/sq)	Resistivity ($\Omega\text{ cm}$)	Mobility ($\text{cm}^2/\text{V s}$)	Carrier density (cm^{-3})
SnO ₂ :F	0.5	7.29	3.65×10^{-4}	22.7	7.54×10^{20}
ZO48 (center)	1.56	2.47	3.87×10^{-4}	40.1	4.03×10^{20}
ZO48 (edge)	1.04	3.47	3.61×10^{-4}	43.3	4.00×10^{20}
ZnO:Al ¹³	N/A	N/A	1.40×10^{-4}	34.0	1.30×10^{20}

TABLE II. CdS/CdTe device data on SnO₂:F and ZnO:Al.

TCO	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)	Series resistance ($\Omega\text{ cm}^2$)	Shunt resistance ($\Omega\text{ cm}^2$)
SnO ₂ :F	820	20.7	73.96	12.6	3.9	1822
ZnO:Al	814	23.6	73.25	14.0	3.16	989

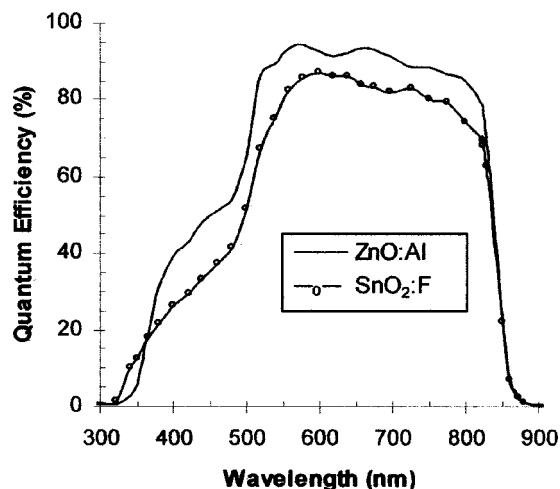


FIG. 3. QE curves of CdS/CdTe solar cells on ZnO:Al and SnO₂:F.

ciency we have achieved using ZnO:Al as the front contact to a superstrate-configuration CdS/CdTe cell. It is also the highest efficiency for an all-sputtered CdS/CdTe solar cell.

Figure 3 shows the quantum efficiencies (QEs) of both devices, measured at NREL. The QE of the ZnO:Al-based device is lower in the 300–340 nm region due to lower band gap of ZnO:Al in comparison to SnO₂:F TCO. The figure clearly shows that the ZnO:Al-based cell has a higher collection in the blue region (360–560 nm) even though the deposited CdS was 0.13 μm in both cases. The QE in the longer-wavelength region (820–860 nm) shows the absorption edge of the modified absorber, CdTe_{1-x}S_x obtained due to interdiffusion of some CdS into CdTe during CdCl₂ treatment. The similar response in this region indicates that CdS diffusion is similar in both cases, and therefore the higher QE response in the blue region is truly due to better transmission of the TCO/ASG. However, the ZnO:Al/CdS interface could also have been modified during the CdCl₂ treatment because of some interdiffusion of Zn into CdS, increasing the band gap and transmittance of CdS similar to interdiffusion between the Zn₂SnO₄/CdS interface,¹⁴ and hence contributing to enhanced photoresponse in the 400 to 500 nm region. The higher QE response (by $\sim 11\%$) of the ZnO:Al based device in the visible region (550–825 nm) is clearly due to better transparency of ZnO:Al TCO in the visible region.

The stability of CdS/CdTe devices on both types of TCOs was also studied under one-sun simulated illumination at $\sim 55^\circ\text{C}$ and open-circuit conditions. The light soak appeared to trigger different degradation mechanisms for cells on the two types of TCOs during the initial days of stressing. The initial fast change in ZnO:Al-based devices caused a degradation in efficiency by 42.7% in 40 days of stressing which is almost double the degradation (21.7%) in efficiency of the SnO₂:F-based devices for the same duration of light soak. The corresponding degradation in V_{OC} , J_{SC} , and FF for ZnO:Al and SnO₂:F based devices were 14.2%,

18.3%, and 18%, and 6.3%, 9.3%, and 8%, respectively. We suggest that the initial fast degradation in ZnO:Al-based devices could be due to the lower thermal stability of ZnO:Al layer and/or interdiffusion across the ZnO/CdS interface occurring during processing and light soaking.

ZnO:Al films on ASG were used to fabricate a 14% CdS/CdTe solar cell without using an antireflection coating, a high resistivity buffer layer, or thinning the CdS layer. The improvement in efficiency was mainly due to lower sheet resistance and higher transmission of the ZnO:Al TCO which increased the short-circuit current density by 15%. We believe that the 14% cell efficiency is highest using a ZnO:Al front contact, and also for any CdS/CdTe solar cell in which all semiconductor layers are prepared by sputtering. This result confirms that the moderate temperatures needed for the magnetron sputtering process can provide important advantages in cell fabrication and expand the range of materials available for thin-film polycrystalline solar cells.

In comparison to sputtered cells on commercial SnO₂:F, the stability of ZnO:Al-based cells is poorer. We believe this may be due to interdiffusion across the ZnO:Al/CdS interface. The use of a highly resistive ZnO buffer layer on conducting ZnO:Al is expected to improve the stability and would also permit the use of thinner CdS layers to achieve improved performance.

The help of Dr. Sung Hyun Lee and Yang Yu in the measurements of optical and electrical properties are appreciated. This work was supported by the High Performance PV Program of NREL (Martha Symko-Davies) and the Thin Film Photovoltaic Partnership Program of NREL (Ken Zweibel).

¹J. Britt and C. Ferekides, Appl. Phys. Lett. **62**, 2851 (1993).

²X. Wu, J. C. Keane, R. G. Dhere, C. DeHart, D. S. Albin, A. Duda, T. A. Gessert, S. Asher, D. H. Levi, and P. Sheldon, *Proceedings of the 17th European Photovoltaic Solar Energy Conference* (2001), pp. 995–1000.

³A. N. Tiwari, A. Romeo, D. Baetzner, and H. Zogg, Prog. Res. Appl. **9**, 211 (2001).

⁴G. Gordillo, M. Grizalez, L. C. Moreno, and F. Landazabal, Phys. Status Solidi B **220**, 215 (2000).

⁵A. Romeo, A. N. Tiwari, H. Zogg, M. Wagner, and J. R. Gunter, *Proceedings of the Second World Conference and Exhibition on Photovoltaic Solar Energy Conversion* (1998), pp. 1105–1108.

⁶L. C. Moreno, J. W. Sandino, N. Hernandez, and G. Gordillo, Phys. Status Solidi B **220**, 289 (2000).

⁷M. Shao, A. Fischer, D. Grecu, U. Jayamaha, E. Bykov, G. Contreras-Puente, R. G. Bohn, and A. D. Compaan, Appl. Phys. Lett. **69**, 3045 (1996).

⁸J. C. Manifacier, J. Gasiot, and J. P. Fillard, J. Phys. E **9**, 1002 (1976).

⁹S. Jafar, C. S. Ferekides, and D. L. Morel, J. Vac. Sci. Technol. A **13**, 2177 (1995).

¹⁰Pilkington Plc, North America, Toledo, OH.

¹¹T. J. Coutts, D. L. Young, and X. Li, MRS Bull. **8**, 58 (2000).

¹²K. Von Rottkay, and M. Rubin, Mater. Res. Soc. Symp. Proc. **426**, 449 (1996).

¹³Y. Igasaki and H. Saito, J. Appl. Phys. **70**, 3613 (1991).

¹⁴X. Wu, R. Ribelin, R. G. Dhere, D. S. Alvin, T. A. Gassert, S. Asher, D. H. Levi, A. Mason, H. R. Moutinho, and P. Sheldon, *Proceedings of the 28th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 2000), p. 470.