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NOTICE

ZNO:AL DOPING LEVEL AND HYDROGEN GROWTH AMBIENT EFFECTS ON CIGS SOLAR CELL PERFORMANCE

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ABSTRACT

Cu(ln,Ga)Se$_2$ (CIGS) photovoltaic (PV) cells require a highly conducting and transparent electrode for optimum device performance. ZnO:Al films grown from targets containing 2.0 wt.% Al$_2$O$_3$ are commonly used for this purpose. Maximum carrier mobilities of these films grown at room temperature are ~20-25 cm^{2}V^{1}s^1. Therefore, relatively high carrier concentrations are required to achieve the desired conductivity, which leads to free carrier absorption in the near infrared (lR). Lightly doped films (0.05-0.2 wt.% Al$_2$O$_3$), which show less IR absorption, reach mobility values greater than 50 cm^{2}V^{1}s^{-1} when deposited in H$_2$ partial pressure. We incorporate these lightly doped ZnO:Al layers into CIGS PV cells produced at the National Renewable Energy Laboratory (NREL). Preliminary results show quantum efficiency values of these cells rival those of a past world-record cell produced at NREL that used 2.0 wt.% Al-doped ZnO films. The highest cell efficiency obtained in this trial was 18.1%.

INTRODUCTION

CIGS PV cells incorporate a transparent conducting oxide (TCO) layer as their top electrode. ZnO:Al targets containing 2.0 wt.% Al$_2$O$_3$ are commonly used for this purpose because ZnO:Al offers acceptable electrical and optical properties when grown using the low substrate temperatures preferred for the final steps of CIGS device processing. Other common TCO's, such as In$_2$O$_3$:Sn, can offer higher electrical and optical performance, but only at higher deposition temperatures. Maximum mobilities of ZnO:Al films grown from targets containing 2.0 wt.% Al$_2$O$_3$ at room temperature are ~20-25 cm^{2}V^{1}s^1. High carrier concentrations or thick films are therefore required to achieve the desired sheet resistance. However, high TCO conductivity is best achieved by increasing mobility rather than carrier concentration for PV device applications [1]. High carrier concentration produces high infrared (IR) free carrier absorption, while high mobility reduces free carrier absorption. In this study, we investigate the extent to which lighter Al doping coupled with H$_2$ incorporation in the Ar sputtering ambient can improve ZnO:Al film electrical and optical properties for utilization in PV devices. We examine undoped ZnO and ZnO:Al films grown by RF magnetron sputtering from targets with Al$_2$O$_3$ contents from 0.05 to 2.0 wt.%. Mobility values exceed 50 cm^{2}V^{1}s^1 for films containing 0.05 — 0.2 wt.% Al$_2$O$_3$ when grown at substrate temperatures up to 200°C. IR transmittance is increased strongly at these lower Al levels compared to that of the standard 2.0 wt.% Al$_2$O$_3$ films.

EXPERIMENTAL DETAILS

TCO films were deposited by radio frequency (RF) magnetron sputtering at 13.56 MHz using a Unifilm Technology PVD-300 system in a sputter-down configuration with a source-to-substrate distance of ~1.5 cm. Targets, purchased from CERAC, Inc. (Milwaukee, WI), were hot-pressed to 3-inch planar form. The undoped ZnO target was stated as 99.999% pure by the vendor. The ZnO:Al targets, of 99.995% purity, contained 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 wt.% Al$_2$O$_3$. Corning 7059 and 1737 glass substrates were soaked for 3 hours in a mechanically stirred solution of 1% detergent (Liqui-Nox) in deionized water maintained at ~90°C, subsequently rinsed in two tanks of clean deionized water, and allowed to dry in air. A radiative boron nitride heating element permitted substrate temperatures up to ~360°C. A cryopump established chamber base pressures between 4x10^{-8} and 2x10^{-7} Torr prior to deposition. Ar, H$_2$, and O$_2$ gas flows were controlled with needle valves and measured using an ion gauge. Chamber pressure was throttled to 15 mTorr during deposition as measured by a capacitive manometer. Sputtering was performed in constant power mode at 72 W (with corresponding voltage ~100 V) to deposit films to a nominal thickness of 500 nm. Substrates were allowed to equilibrate on the heater for one hour prior to deposition and allowed to cool for 45 minutes in the sputtering ambient after deposition. Thickness measurements were performed by stylus profilometry (Veeco Dektak) and spectroscopically (190—1000 nm; n&k Technology model 1280 Analyzer). Carrier concentration, mobility, and resistivity were obtained at room temperature from Hall analysis using the van der Pauw method (BioRad HL5500). Optical reflectance and transmittance were obtained using a spectrophotometer (Cary 5G) with integrating sphere (Labsphere DRA-CA-50).

CIGS photovoltaic cells were grown on 2-mm-thick soda lime glass with a 1 μm-thick layer of Mo deposited by sputter deposition. The CIGS absorber layer was deposited to a nominal thickness of 2.5 pm using a 3-stage process [2]. In place of the commonly used CdS layer, a bilayer of CdS and ZnS was formed by chemical bath deposition on one of the samples. ZnO:Al depositions on these devices are discussed below.

RESULTS AND DISCUSSION

ZnO:Al Studies

Based on initial studies of highly-doped films deposited in 100% Ar [3], a substrate temperature of 200°C was chosen for sputtering ambient studies. The effects of ambient were investigated by adding small amounts of O_2 or H_2 to the Ar sputtering gas.

When O_2 is added to the Ar ambient, carrier concentration decreases sharply for all Al_2O_3 levels (Fig. 1). The most significant decrease occurs for the undoped ZnO because it contains no potentially ionized extrinsic dopant species to contribute carriers. Mobility values also decrease significantly when small amounts of O_2 are added to the ambient regardless of Al doping level.
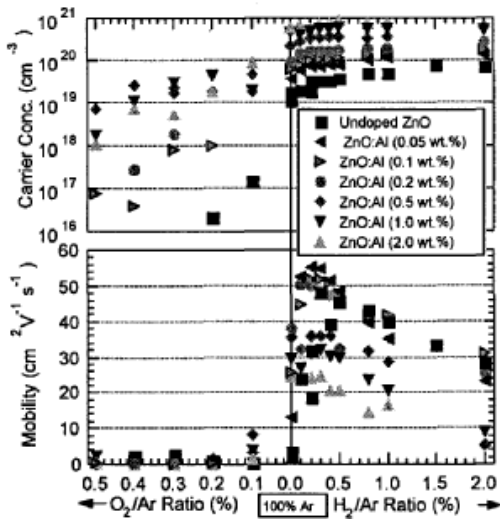

Fig. 1. Carrier concentration (upper panel) and mobility (lower panel) vs. O_2/Ar ratio (left) and H_2/Ar ratio (right) of the sputtering gas for depositions performed at 200°C.

These decreasing values could have a number of causes. Because these films are polycrystalline, with an average grain size of ~30 nm [3], the grain boundary density is high. O_2 may adsorb on these grain boundaries [4-7]. Adsorbed O could remove free carriers from the exterior of the grains (and thus from the conduction band) to become O^- [4], reducing the measured carrier concentration. Trapped charge due to the adsorbed O^- would establish electrostatic potential energy barriers that could inhibit carrier transport between grains, lowering the measured Hall mobility [6]. Other mechanisms may also describe this behavior. O vacancies (V_O) and Zn interstitials (Zn_i) have been suggested as providers of carriers in ZnO [8-111]. Addition of 0_2 to the ambient, therefore, could fill V_O or decrease the number of Zn_i formed, decreasing the number of free carriers. Other workers have suggested, however, based on density functional theory calculations [12-15], that neither of these latter mechanisms likely provide carriers in ZnO. Calculations indicated that V_O are deep donors, while Zn_i

have a low activation energy for diffusion from their interstitial sites [13]. In recent years, H has been suggested as a source of carriers in ZnO [16-22]. The addition of O_2 to the growth ambient could remove beneficial effects (detailed below) of any residual H in the growth chamber.

Controlled amounts of H_2 increase both carrier concentration and mobility (Fig. 1). Carrier concentration values for films grown in a H_2-rich ambient increase systematically from I to 8×10^{20} cm^{-3} as the Al_2O_3 content of the target increases from 0.05 to 2.0 wt.%, respectively. The highest mobilities, particularly for undoped and lightly Al doped films, were obtained when a small amount of H_2 was added to the Ar sputtering ambient (optimal H_2/Ar ~0.3%). Remarkably, films containing 0.05 - 0.2 wt.% Al_2O_3 exceed the mobility of undoped ZnO, reaching values greater than 50 cm^2√s^{-1} near 0.3% H_2/Ar.

H_2 added to the sputtering ambient could form complexes with adsorbed O^- on ZnO grain boundaries, causing the O to be removed or passivated. This could return carriers to the conduction band, increasing the carrier concentration. The size of electrostatic barriers between grains would also be reduced, increasing the measured Hall mobility. Alternatively, the use of H_2 enables a reducing environment that could be more conducive to the formation of V_O and Zn. The decrease in mobility with larger amounts of Al_2O_3 and with excessive H_2 content (>0.3% H_2/Ar) is likely due to increased ionized or neutral impurity scattering because both Al and H constitute scattering centers.

Differences in the substrate temperature dependence of electrical properties were observed between films grown in the 100% Ar and 0.3% H_2/Ar ambients when using the 0.2 wt.% Al_2O_3 target (Fig. 2). Films grown in 100% Ar display a broad maximum in both carrier concentration and mobility at 150-200°C, whereas films
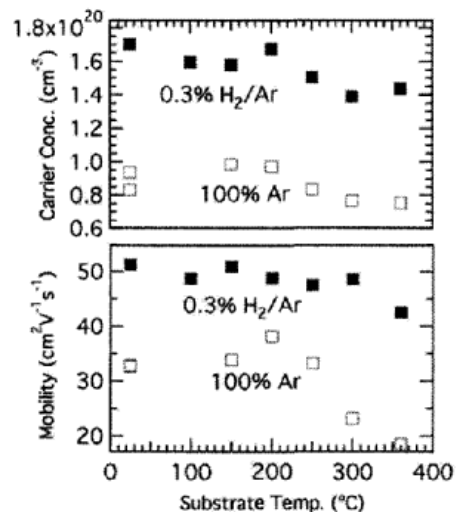

Fig. 2. Carrier concentration (upper panel) and mobility (lower panel) vs. substrate temperature for films grown in 100% Ar and 0.3% H_2/Ar from the 0.2 wt.% Al_2O_3 target.

grown in 0.3% H_2/Ar show a slight monotonic decrease in both values with increasing substrate temperature. Thus, lightly doped ZnO:Al films with the best electrical properties can be obtained by room temperature deposition in a 0.3% H_2/Ar partial pressure ambient, without the need for substrate heating. This low temperature deposition is ideal for utilization in CIGS PV devices that require processing temperatures below ~200°C to prevent degradation. Note that the addition of H_2 increases both mobility and carrier concentration over a wide range of deposition temperatures, which improves manufacturability and process robustness.

Optical transmittance data (Fig. 3) show that films of all Al doping levels have visible transmittance values of ~85% on average. Higher Al doping reveals a systematic increase in bandgap with increasing carrier concentration from its intrinsic value of ~3.3 to ~3.8 eV. The lightly doped films show significantly less IR absorption than the films with higher Al content. Although this is due primarily to the lower carrier concentration of these films, the higher mobility of films with lower Al content also reduces IR absorption [1]. Because high transparency up to ~1100 nm is required for CIGS PV devices, we believe lowering the Al content is a promising avenue toward improved device performance.
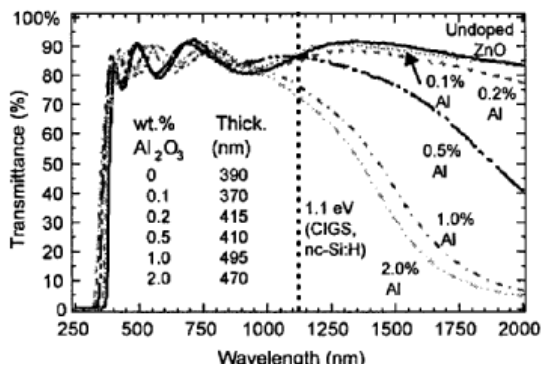

Fig. 3. Transmittance vs. wavelength for the highest mobility film at each Al_2O_3 level, deposited at 200°C in 0.3% H_2/Ar (except for the 2.0 wt.% Al_2O_3 film, deposited in 100% Ar). The CIGS bandgap appears for comparison.

Implementation on CIGS Devices

To test whether ZnO:Al films with lower Al content might be used successfully in CIGS PV devices, two samples from the same CIGS deposition were selected. CIGS samples were grown to a nominal thickness of 2.5 pm using a 3-stage process [2] on 2-mm-thick soda lime glass with a 1-µm-thick layer of Mo deposited by sputter

deposition. One sample was processed with a bilayer of CdS and ZnS, while the other received the standard CdS treatment by chemical bath deposition. The bilayer was used to preserve the beneficial qualities of the CdS/CIGS interface while improving the transparency of this layer at lower wavelengths. The CdS/ZnS sample was coated with 50 nm of intrinsic ZnO (i-ZnO) deposited at room temperature in 100% Ar and 190 nm of ZnO:Al deposited from a target containing 0.1 wt.% Al_2O_3 at room temperature in 0.3% H_2/Ar. The CdS-treated sample, receiving the standard processing, was coated with 100 nm of i-ZnO and 120 nm of ZnO:Al deposited from a target containing 2.0 wt.% Al_2O_3 at room temperature in 100% Ar. Each sample received a MgF_2 anti-reflection coating and was patterned using photolithography into 0.42 cm devices. The performance of the device utilizing ZnO:Al containing 0.1 wt.% Al_2O_3 compares favorably with the highest-efficiency device produced from the CdS-treated control sample using the standard ZnO:Al deposition (Table 1). The slightly lower fill factor for the 0.1 wt.% Al_2O_3 device (with the CdS/ZnS bilayer) is likely due to the higher series resistance of ZnS than CdS. The open-circuit voltage values for the two devices are comparable within the measurement uncertainty. The slightly higher short-circuit current for the 0.1 wt.% Al_2O_3 device (with the CdS/ZnS bilayer) is attributed to improved transparency of this layer compared to the typical CdS layer.

The absolute external quantum efficiency (QE) of the device utilizing ZnO:Al containing 0.1 wt.% Al_2O_3 was compared to that of the 19.5% NREL CIGS device that held the world record (WR) until recently (Fig. 4).
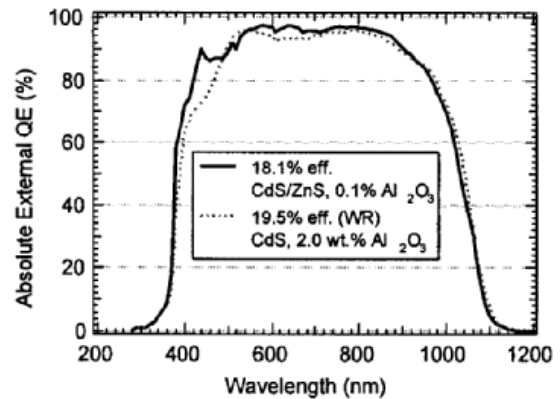

Fig. 4. External quantum efficiency (QE) vs. wavelength for CIGS device utilizing ZnO:Al containing 0.1 wt.% Al_2O_3 (18.1% efficiency) compared to QE of the past world-record (WR) 19.5% NREL CIGS device using 2.0 wt.% Al_2O_3.

Table 1. CIGS PV devices incorporating lightly doped (0.1 wt.% Al_2O_3) and standard (2.0 wt.% Al_2O_3) ZnO:Al.

Al_2O_3 Content (wt.%)	Treatment	Efficiency (%)	Fill Factor (%)	Open-circuit Voltage (mV)	Short-circuit Current (mA/cm^2)
0.1	CdS/ZnS	18.1	76.2	671	35.4
2.0	CdS	18.1	79.1	666	34.4

Differences in QE at the lower wavelengths are primarily due to the transparency difference between the CdS/ZnS bilayer (used on the 0.1 wt.% Al_2O_3 device) and CdS layer (on the 2.0 wt.% Al_2O_3 WR device). At the higher wavelengths, the device produced with the ZnO:Al containing 0.1 wt.% Al_2O_3—in one trial, without optimization—demonstrates QE meeting or exceeding that of the record device through much of the higher wavelength range. These findings suggest that, with optimization of the device processing to take advantage of the higher ZnO:Al mobility, utilization of the lightly-doped ZnO:Al may result in higher device performance.

CONCLUSIONS

Lighter Al doping, when combined with controlled incorporation of H_2 in the sputtering ambient, produces ZnO:Al films with higher near-IR transmittance and carrier mobility values compared to those grown using the more typical 2.0 wt.% Al_2O_3. In addition, H_2 incorporation increases both mobility and carrier concentration over a wide range of deposition temperatures, including room temperature, improving manufacturability and process robustness. For these reasons, lightly doped ZnO:Al films grown in a controlled H_2 partial pressure ambient at room temperature may offer advantages over films with higher Al concentrations deposited in 100% Ar, particularly where low-temperature deposition is a requirement.

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