

TRANSPARENT CONDUCTING ZNO FILMS BY REACTIVE DC MAGNETRON SPUTTERING FROM METALLIC TARGETS

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We report on our efforts to deposit transparent, conducting, zinc oxide films by reactive sputtering from metallic zinc and dopant (aluminum or indium) targets in an argon/oxygen gas mixture. Several methods have been used to include dopant atoms including: 1) placing pieces of Al over the Zn target, 2) sputtering from a Zn₉₈Al₀₂ alloy target, and 3) deposition of multilayer ZnO/In₂O₃ structures. The best results were achieved using Method (1) with Al covering ~20% of the Zn target. Resulting films were highly transparent and had resistivities of 0.9 mΩ·cm. Method (2) was not successful. Method (3) showed promise, but appears to require thinner layers than we are able to currently achieve.

Keywords: ZnO, Thin Film, Sputtering, PV Materials, CuInS₂, Deposition, Optical Properties

1 INTRODUCTION

Thin film solar cells are of considerable interest for their potential for inexpensive and versatile photovoltaic modules for terrestrial power-generating applications. They also offer promise for development lightweight solar cells for space applications. Copper-indium-diselenide (CuInSe₂ or CIS) and related compounds have been employed as absorber layers in heterojunction, thin-film solar cells with considerable success. These p-type absorber layers are combined with n-type, wide-bandgap semiconductors to complete the p-n junction. Sunlight passes through the wide-bandgap semiconductor, or window layer, to be absorbed in the CIS layer very close to the physical junction.

Ideally the window layer would be highly conducting and transparent for wavelengths that make up the solar spectrum. Zinc-oxide (ZnO), with a 3.3 eV bandgap energy, has emerged as the window layer of choice for CIS solar cells. The best CIS solar cell performance has been achieved using a window layer that consists of a thin (50-60 nm) layer of CdS, a thin (90 nm) layer of i-ZnO, followed by a thicker (120 nm), heavily doped layer n-ZnO layer [1]. The CdS layer is typically deposited in a chemical bath while the ZnO bilayer is typically deposited by RF-sputtering from an Al- or Al₂O₃-doped, ZnO target while varying the O₂/Ar ratio of the sputter gas mixture. In general better results are achieved when the ZnO is deposited at elevated temperatures. High-efficiency CIS solar cells can tolerate 200°C substrate temperatures with negligible degradation [2].

We are engaged in the development of thin film copper-indium-disulfide (CuInS₂) solar cells on lightweight flexible substrates for space applications [3]. As part of this effort we are exploring alternate methods for depositing ZnO window layers. Here we have used reactive sputtering from a metallic Zn target. This technique was chosen both for its potentially high deposition rate and also because of the availability of equipment.

2 LITERATURE REVIEW

Metallic films are readily deposited using dc

magnetron sputtering from a metal target using pure argon (Ar) for the sputter gas. Reactive sputtering of the metal oxide from the metal target is accomplished by using a mixture of Ar and oxygen (O₂) for the sputter gas [4]. For a low O₂/Ar ratio metal oxide is included in the deposited film while the target itself remains metallic. But as the O₂ partial pressure increases the target surface oxidizes and becomes insulating, which leads to an unstable plasma. The O₂/Ar ratio and substrate temperature are key parameters for controlling film properties.

DC reactive magnetron sputtering of ZnO films has received some attention in the literature, mainly because of its potentially high deposition rates. Various groups have achieved films ~1 μm thick with greater than 80% transmission and resistivities below 1 mΩ·cm. Jin, et al. co-sputtered Al-doped ZnO films using simultaneous rf sputtering from a ZnO target with dc reactive sputtering from an Al target [5]. Appropriate mixing was achieved by rotating the substrate past each target at 150 rpm. Ye and Tang deposited In-doped films using dc reactive sputtering from a Zn target containing small pieces of In [6]. High mobility Al-doped films were achieved by Shöffler and Schock by dc reactive sputtering from a Zn:Al target onto substrates held at 450°C [7].

Zafar et al. have used the technique to deposit both Al- and F-doped ZnO films [8]. They achieved Al-doping by placing Al pieces on a Zn target and F-doping by introducing CF₄ into the sputter gas. Substrates were held at temperatures ranging from 150-350°C during deposition. They found the location of the substrate relative to the plasma to significantly affect the outcome.

Elimer and Wendt deposited Al-doped films from metallic Zn:Al targets using both rf and dc magnetron reactive sputtering [9]. Szyszka and Jäger deposited both In- and Al-doped films using rf reactive magnetron sputtering from Zn:In and Zn:Al targets. By varying the oxygen flow they explore the target voltage that results in the metallic mode (low oxygen), transition mode, and oxide mode (high oxygen) [10]. Szyszka reported that transparency was achieved at minimum substrate temperatures of 100°C due to desorption of surplus Zn [11]. Gillespie et al. developed a strategy for controlling oxygen flow on target voltage for depositing Al-doped films from a metallic Zn:Al target [12]. Fenske et al.

have co-sputtered Al-doped films from metallic Zn and Al targets [13]. Mixing of species was accomplished by mounting the two sputter guns in confocal positions.

Most recently Chen et al. have deposited Al-doped films from single Zn:Al targets. They find nearly an order of magnitude lowering of resistivity when substrate temperature is increased from 100 to 200°C [14].

3 DEPOSITION SYSTEM

For this work we have modified a vacuum metallization system consisting of a conventional diffusion-pump/cold trap, 18-in vacuum chamber with two, Sloan S-310 dc magnetron sputter guns (S-guns). Sputter targets consist of 3 in. (7.6 cm) diameter x 0.93 in. (2.4 cm) metallic rings, typically 1/16 to 1/8 in thick (1.6 to 3.2 mm). Ring targets were press fit into standardized aluminum holders for ready insertion into the S-guns. The two S-guns sputter up from the base plate of the chamber. Substrates are mounted above the targets on a copper heated stage attached to a motorized positioner allowing samples to be moved back and forth over either of the two targets. One S-gun is powered by a Sloan *Mag-2* dc power supply (I_1 , V_1) while the other is powered by a Xantrex *XFR 600-2* dc power supply (I_2 , V_2). Ar (F_A) and O₂ (F_{O_2}) gas flow rates are controlled by separate MKS mass flow controllers connected to an MKS *model 247*, 4-channel readout and chamber pressure (p) is measured with a 0-50 mTorr, MKS baratron capacitance manometer connected to an MKS *model PR-4000* controller. A variable conductance valve located below the liquid nitrogen trap in the pumping port of the diffusion pump is used to throttle pumping speed to maintain $p \approx 15$ mTorr during deposition. Ar(g) is plumbed through the bottom of each S-gun while O₂(g) is fed through the side of the chamber to reduce target oxidation. The sputter geometry is shown in Figure 1. The heated sample stage sits over the open square hole on the outbound end of the sample positioner. The positioner may be rotated to move the stage anywhere along the semicircle. The bottom surface of the sample stage is 6.5 cm above the top of the base plate.

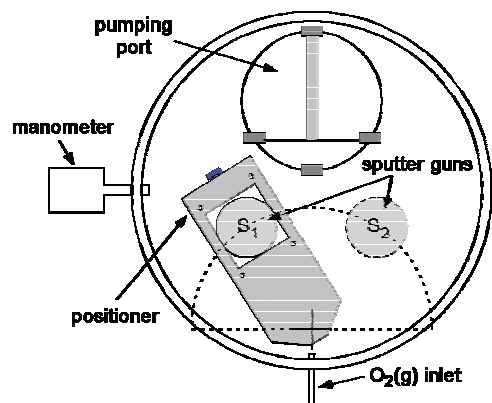


Figure 1: Overhead view of the chamber base plate.

A personal computer controls all aspects of the deposition process. Control of the *Xantrex* supply is achieved using RS-232 protocols. Communication with other instruments is accomplished with combinations of analog and digital i/o from two data acquisition (DAQ) boards in the computer. The motorized positioner and the Sloan power supply communicate with the DAQ

through home-made interface circuits. The computer directly controls gas flows F_A and F_{O_2} , sputter currents I_1 and I_2 , and the positioner stepper motor's speed and direction. The computer also reads various sensors including five optical switches and an analog voltage associated with sample position, sputter target voltages V_1 and V_2 , and chamber pressure p . Control software has been written to move the positioner to desired locations and to adjust flow rates F_A and F_{O_2} to maintain a desired pressure. Software allows the user to set up a deposition control sequence obtained from successive lines of an input file.

4 EXPERIMENTAL METHOD

Most films were sputtered onto *Corning 2947* 1 in. x 3 in. (2.54 cm x 7.62 cm) glass microscope slides. Four-probe resistance measurements using alternating current and lock-in amplifiers were used to determine film sheet resistance. X-ray goniometer scans were performed using a *Philips X'Pert* X-ray diffractometer. Film thicknesses were determined with a *Sloan DecTak II* profilometer. Transmission and reflection properties for wavelengths 200-2000 nm were performed using a *Perkin-Elmer Lambda 19* UV-vis-NIR spectrometer. In some cases Hall measurements were performed with a *Bio-Rad HL5500PC* system operated in the 4-probe, Van der Pauw configuration.

5 UNDOPED FILMS

Insulating, highly transparent ZnO films are readily deposited from a 99.99% pure metallic Zn target for a range of Ar/O₂(g) flow rates and substrate temperatures. Figure 2 shows the optical transmission spectrum for sample Zn-007. This 400-nm-thick film was deposited at room temperature with an Ar/O₂ flow ratio of 2 and a pressure of 12.7 mTorr.

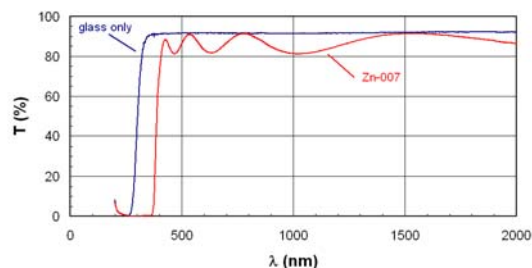


Figure 2: Transmission spectra for intrinsic ZnO film Zn-007 on glass and the naked glass slide.

With less oxygen (i.e., higher Ar/O₂ ratio) at room temperature the resulting film becomes brownish in color, loses transparency, and slightly conducting. At elevated substrate temperature film transparency is restored, allowing deposition of intrinsic ZnO with less oxygen. We routinely deposit transparent ZnO with an Ar/O₂ flow ratio of 4:1 with the substrate held at 100°C. A typical XRD spectrum for such a film is shown in Figure 3.

6 DOPED FILMS

We have explored three different methods for doping ZnO films: 1) placing pieces of Al over portions of the Zn target during deposition, 2) depositing from a Zn₉₈Al₀₂ alloy target, 3) and depositing alternating layers

from a pure Zn and pure In (or Al) targets. So far method 1 has resulted in the best films. The results are discussed below.

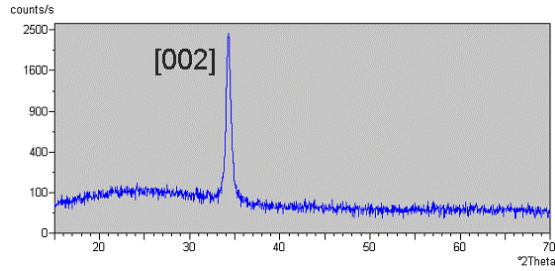


Figure 3: XRD spectra for 300-nm-thick i-ZnO film WT-059. The peak at $2\theta = 34.5^\circ$ shows the [002] preferential orientation typical for ZnO on glass.

6.1 Method 1: Aluminum pieces on Zn target

Two 1-in (2.5 cm) wide aluminum strips were mounted on the inside of the Zn target, covering roughly 20% of the target area. Films sputtered at room temperature with an Ar/O₂ ratio of 2 were transparent and non-conducting. Reducing O₂ flow resulted in both increased conductivity and reduced transparency. Transparency was improved by raising substrate temperature. Highly conducting yet transparent films were achieved with an Ar/O₂ flow ratio of 8 and the substrate held at 200°C. Figure 4 shows the results of optical measurements for film Zn-041 deposited with this method. The film had a thickness of 0.74 μm and a sheet resistance of 12 Ω/sq, corresponding to a resistivity of 0.9 mΩ-cm. This resistivity is three times that for the best films reported by Shäffler and Schock [7].

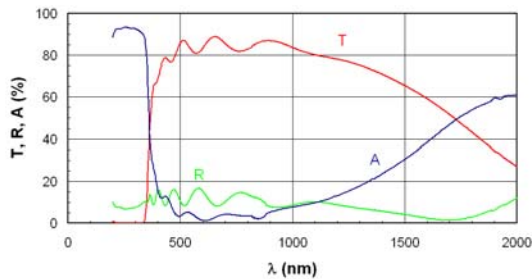


Figure 4: Transmission (T), reflectance (R), and absorbance (A) spectra for 0.70 μm thick doped ZnO film Zn-041 fabricated with Method 1.

6.2 Method 2: Alloy Zn target

While films deposited with Method 1 were highly conducting, the doping profile was not uniform. In practice it proved difficult to evenly distribute many Al pieces on the ring target. We therefore decided to purchase an alloy target consisting of 98% Zn and 2% Al. Several groups report success at fabricating doped ZnO films by reactive sputtering from such targets. [7, 9, 10, 12]

Despite numerous attempts we were unable to achieve films that were both transparent and conducting with this target. All combinations of substrate temperatures (up to 200°C) and O₂ flow rates resulted in films that were either transparent and insulating or conducting and opaque. The work was abandoned in favor of Method 3 below.

6.3 Method 3: Alternating layers

With the completion of the motorized substrate positioner and the acquisition of the second, Xantrex power supply we obtained the capability to simultaneously sputter from two targets while moving the substrate between them. Transit time between two targets is about 8 seconds. The initial intent was to deposit many alternating layers of ZnO and Al (or Al₂O₃) so as to achieve the desired overall stoichiometry. For sufficiently high temperature and sufficiently thin layers interdiffusion should yield a homogenous structure.

During Al calibration depositions we immediately experienced instabilities associated with oxidation of the target [15]. Al was subsequently abandoned in favor of In as a dopant. The In target's behavior with O₂ was found to be similar to that of the Zn target.

A series of layered films were deposited as indicated in Table I. All films were deposited with a working gas pressure of 15.0 mTorr, Ar/O₂ flow ratio of 4.0, substrate temperature of 100°C, and target currents of 200 mA.

Table I: Summary of ZnO/In₂O₃ layered film. N represents the number of “film pairs.” The times are given for the time spent over the Zn and In targets for each film in a pair. d represents total film thickness and R_{SH} is the sheet resistance.

Film #	Zn		In		d (nm)	R _{SH} (Ω)	
	N	Δt (s)	V (V)	Δt (s)			V (V)
51	1	1800	255-265	-----	270	> 10 ⁶	
52	15	120	268-272	-----	270	> 10 ⁶	
54	8	120	250-308	120	275-292	309	-----
55	12	120	260-320	40	275-300	299	-----
57	14	120	305-330	17	273-300	293	-----
64	1	-----	-----	1800	305	310	6 x 10 ⁵
65	14	120	262-96	17	291-306	293	> 200
67	1	-----	-----	1800	281	310	> 10 ⁶
68	1	1800	270-281	-----	270	> 10 ⁶	

Undoped ZnO films 51, 52, and 68 were deposited with 30 min. total time over the Zn target and without In. Films 51 and 68 were deposited in a single layer while film 52 was deposited in 15 interrupted layers, with the positioner moving the substrate over the In gun and back in-between ZnO layers. The three films are nearly identical; all are transparent and non-conducting. XRD data for all three are similar to that shown in Figure 3 demonstrating the [002] film orientation. Film 64, entirely In₂O₃, was also transparent and non-conducting.

Layered films 54, 55, and 57 were fabricated with successively thinner In₂O₃ layers. Electron dispersive spectroscopy measurements (EDS) quantified the [In]/[In+Zn] ratios for these films to be 56%, 33%, and 16% respectively. All three films were dark brown and nearly opaque.

Layered film 65 was deposited under conditions identical to 57 except that, during In deposition, the substrate was centered over the inside edge of the In target so as to yield a gradient in In₂O₃ thicknesses along the length of the microscope slide. The resulting film was highly transparent. The slide was subsequently sectioned into six, ½ in. (1.3 cm) segments for characterization as shown in Figure 5. Section F is

expected to have composition similar to film 57 while Section A is expected to contain negligible In.

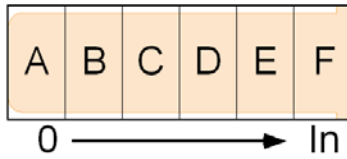


Figure 5: Sectioning of film 65 showing gradient in the In concentration.

Properties of film 65 are summarized in Table II. Section E displayed the lowest sheet resistance. Assuming a film thickness of 300 nm this sheet resistance of $\sim 200 \Omega/\text{sq}$. corresponds to a resistivity of $5 \text{ m}\Omega\text{-cm}$.

XRD measurements on Section A showed the characteristic ZnO [002] peak while measurements on Section F exhibited no X-ray peaks whatsoever. Patterns for films B through E revealed a clear transition between these two.

Table II: Summary of properties of six Sections of film 65. Shown are the sheet resistance and the relative XRD intensities of the [002] ZnO peak.

Section	$R_{\text{SH}} (\Omega)$	[002]
A	2,060	600
B	1,470	340
C	527	140
D	254	80
E	192	66
F	217	30

7 DISCUSSION

DC reactive sputtering from S-guns provides a convenient, rapid method for depositing highly-transparent, insulating ZnO films. Successful doping of films has been accomplished by covering portions of the Zn target with Al. Target, and resulting film non-uniformity poses a challenge. It is difficult to distribute Al uniformly around the ring target and to vary targets so as to optimize Al content. Moreover, target composition will change with use, albeit slowly, and the mixing of Zn and Al metals will complicate reclamation of unused metals in the manufacturing environment.

Reactive sputtering of doped ZnO films using two S-guns appears to have greater potential for control and recycling of unused target materials. For sufficiently thin layers and high substrate temperatures, the layered film technique must result in a homogenous, doped ZnO film. This is confirmed by XRD measurements on In-poor Sections (A and B) of film 65. But clearly the 100°C deposition temperature used was insufficient to promote mixing for In levels appropriate for doping (Section E of film 65). The thicker In_2O_3 layers (Sections C-F) interrupt the ZnO crystal growth resulting in very small crystallite size and random orientation. It is doubtful that appropriate mixing of these layers will be achieved below 200°C , the maximum safe temperature for CIS solar cells.

To achieve mixing at low temperatures requires much thinner layers – and these cannot be achieved with

our slow substrate positioner. A new substrate positioner that rapidly rotates the substrates above both Zn and In guns should yield the desired mixing at low temperatures [5]. Material utilization would not be a problem if one were to simultaneously coat many samples (covering an entire rotating stage). But for the research environment in which one is interested in low throughput, material utilization will be significantly lowered by such a modification to the substrate positioner. Such a positioner also presents challenges for heating the substrate during deposition.

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