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Tailoring electrical and optical properties of Al-doped ZnO thin films grown at room temperature by reactive magnetron co-sputtering: From band gap to near infrared

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ABSTRACT

Al-doped zinc oxide (AZO) thin films were deposited at room temperature (RT) using reactive magnetron co-sputtering of two metallic Zn and Al targets in the presence of oxygen. The structural, optical and electrical properties of the AZO thin films were tailored by varying the Al content through changing Al sputtering power from 0 to 30 W. The AZO thin films deposited at the optimal deposition conditions with Al power of 26–28 W exhibited high transparency in the visible range, shorter plasma wavelength, lower electrical resistivity, lower transmittance and higher reflectance in the near IR range. The results domenstrate that the Al-doping content is strongly correlated to the band gap, electrical and near infrared optical properties using various characterization techniques. Tailoring the infrared optical properties of AZO films can be achieved and applied for desired optical coating applications.

1. Introduction

Transparent conducting oxides (TCOs) have been widely used in microelectronic and optoelectronic devices, such as transparent conducting electrodes [1,2], liquid crystal displays [2], organic light-emitting diodes and thin film solar cells [1,3,4] due to their high optical transmittance and low electrical resistivity. They are also excellent materials for energy efficient window coatings [5,6] and heat reflective coatings [3,7–10]. Un-doped, stoichiometric zinc oxide (ZnO) is a semiconductor with a band gap of 3.27 eV [8] and is highly transparent from visible to infrared (IR) wavelengths, but relatively poor in conductivity. With appropriate doping, aluminum-doped zinc oxides (AZO) have displayed highly transparent conductive properties [1,3,4,6]. AZO coatings have many advantages owing to their abundance in raw materials, low cost, non-toxicity, good tailoring of the ultra violet (UV) absorption and their excellent thermal and chemical stability [6]. With adequate Al-doping, transparent conductive AZO films are also good near-infrared (NIR) reflectors [1,3,4], which are useful for less expensive energy-efficient windows, solar cells and optoelectronic display devices. In the past, impurity doped (B-doped, Ta-doped, Ga-doped, In-doped, Al-doped) zinc oxide films were fabricated by many techniques such as electrospraying [11,12], ion plating [13,14], spray pyrolysis [15,16], evaporation [5], pulsed laser deposition (PLD) [17–19], DC magnetron sputtering (DCMS) [4,13,20–24], radio-frequency magnetron sputtering (RFMS) [6], pulse DC magnetron sputtering (PDCMS) [3], and RF and DC magnetron sputtering [2,13]. Most of the reported AZO films were sputtered using a single target such as an AZO target with a fixed Al_2O_3 content [1,3,4,25,26], a Zn-Al alloy target with a fixed Al content [22], a ZnO target with doped metal fragments on it [6,23,27,28], and a Zn target with doped metal fragments [23]. The disadvantages of using a single target are two-fold, it is hard to vary the Al/Zn ratio during deposition without breaking vacuum, but also the deposition rate is relatively low. Independent-control of multiple sources, such as ZnO and Al [6,29], ZnO and Al_2O_3 [30], and multi-metallic (Zn and Al) targets [8–10] have been also used in order to control Al content in the AZO films. Many studies have focused on electrical properties or optical properties in the range (200–900 nm) [24,26], the 200–1000 nm range [29], and the 200–1200 nm range [23]. Most AZO films required relatively high substrate temperatures or post annealing [13,19,20,25,26].

In this work, the AZO films were prepared at room temperature by independent-control of the sputtering powers of Zn and Al targets in a reactive atmosphere to facilitate dynamic adjustment of Al dopant without breaking high vacuum. AZO films with appropriate Al doping provide high transparency in the visible region and while retaining high reflectance in the NIR and IR spectra regions. The optical properties

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Table 1
Deposition parameters used for fabricating the AZO thin films.

Aluminum - DC			Zinc – pulsed DC			$f(O_2)$ (sccm)	P_{O2} (mTorr)
W_{Al} (W)	V_{Al} (V)	I_{Al} (A)	W_{Zn}(W)	V_{Zn} (V)	I_{Zn} (A)		
0	0	0.00	60	255	0.24	1.8	0.2
20	270	0.07	60	258	0.23	1.8	0.1
23	284	0.08	60	258	0.23	1.8	0.1
26	305	0.08	60	259	0.23	1.8	0.1
28	318	0.08	60	259	0.23	1.8	0.1
30	329	0.09	60	260	0.23	1.8	0.1

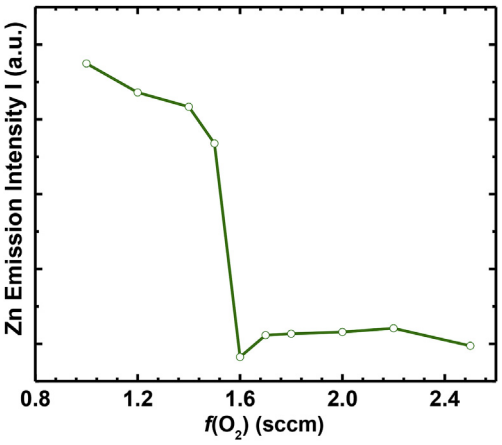

Fig. 1. Emission intensity I of Zn plasma at 307.4 nm as a function of $f(O_2)$.

were studied from the UV to the IR in the wavelength of 200–2500 nm using various characterization techniques. The band gap, electrical and near infrared (NIR) optical properties can be tailored by varying Al sputtering power.

2. Experimental

AZO films were prepared in a customized stainless steel high-vacuum chamber system equipped with multiple magnetron sources using DC magnetron sputtering (DCMS) and pulsed DC magnetron sputtering (PDCMS) techniques. In the current chamber configuration, two magnetron guns are tilted at a 20° angle with respect to the substrate normal, towards the center of the substrate. The chamber was initially pumped down to 50 mTorr by a mechanical roughing pump and further evacuated to a pressure of 2×10^{-7} Torr, or lower, by a Varian turbomolecular pump connected to the chamber via an automated gate valve assembly. Without breaking the vacuum of the chamber, samples were transferred into the chamber through a load lock system. Before

Table 2
AZO film compositions from high energy resolution XPS spectra.

W_{Al} (W)	Al/(Al + Zn) %	Transition	BE (eV)	Composition (at.%)
0	0	C1s	284.8	21.9
		O1s	530.3	41.7
		Zn 2p	1021.9	36.4
		Al 2p	–	–
20	2.1	C1s	284.9	14.0
		O1s	530.4	44.8
		Zn 2p	1021.8	40.5
		Al 2p	74.15	0.78
23	4.0	C1s	284.8	12.8
		O1s	530.5	46.4
		Zn 2p	1021.8	39.5
		Al 2p	74.1	1.34
26	5.6	C1s	284.8	12.2
		O1s	530.4	46.2
		Zn 2p	1021.9	39.4
		Al 2p	74.0	2.12
28	7.5	C1s	284.8	13.4
		O1s	530.5	47.1
		Zn 2p	1021.9	36.8
		Al 2p	74.0	2.64
30	9.1	C1s	284.7	19.2
		O1s	530.5	47.3
		Zn 2p	1021.8	30.7
		Al 2p	73.6	2.86

deposition, 1 inch diameter fused quartz (Machine Glass Specialists Inc.) and silicon (100) prime graded substrate (p-type, University Wafer LLC) were cleaned in acetone, methanol and IPA, dried by nitrogen gas, and then transfered to the chamber.

All AZO films were prepared by reactive magnetron co-sputtering, as described previously in Refs. [31,32]. The Zn target (Plasmaterials, 99.99% purity, 2.00" dia. × 0.250" thick) was placed in a Kurt J. Lesker Torus magnetron gun powered at W_{Zn} = 60 W with a pulse frequency of 80 kHz and a reversed pulse time of 4.5 μs (Pinnacle Plus power supply, Advanced Energy Inc.). An Al target (Kurt J. Lesker, 99.99% purity, 2.00" dia. × 0.250" thick) was placed in a MeiVac MAK magnetron gun powered by an Advanced Energy MDX 500 DC power supply. The power applied to the Al target (W_{Al}) was varied from 20 to 30 W, with one sample fabricated at W_{Al} = 0 W to provide an un-doped ZnO reference sample (Table 1). Research grade argon (99.999%) as a sputtering gas was introduced to the chamber through a port near the magnetron target and was held at 20 sccm constant mass flow rate controlled by an Alicat mass flow meter. The Ar pressure was set at 3 mTorr and then the gate valve position was locked at this position before introducing O_2 into the chamber. Research grade O_2 (99.995%) was introduced through a MKS flow meter into the chamber as a reactive gas through a port near the substrate holder. The O_2 flow rate $f(O_2)$ was fixed at 1.8 sccm for this set of experiments, as determined from the optical emission measurements discussed in Section 3.1 below.

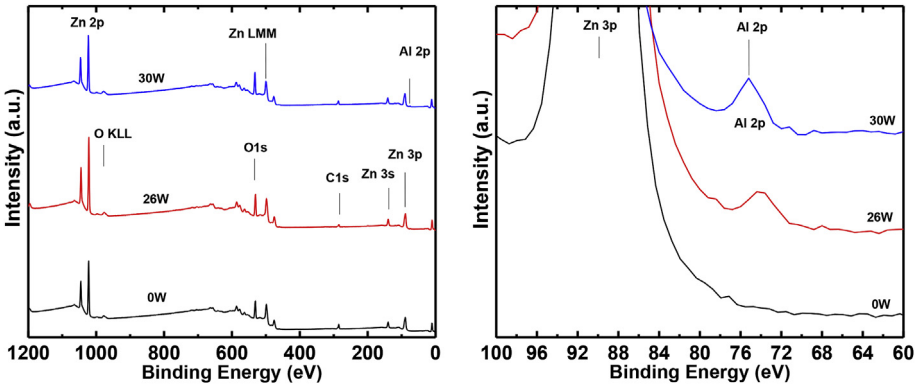

Fig. 2. (left) XPS survey spectra and (right) high energy resolution spectra of the Zn 3p and Al 2p region, (W_{Al} at 0, 26 and 30 W). The spectra are offset for clarity.