Properties of Al-Doped Zinc Oxide and In-Doped Zinc Oxide Bilayer Transparent Conducting Oxides for Solar Cell Applications

M. Marikkannan¹, A. Dinesh¹, J. Mayandi¹,* V. Vishnukanthan²,³ and J. M. Pearce⁴,#

¹Department of Materials Science, School of Chemistry, Madurai Kamaraj University, Tamil Nadu, Madurai-625021, India.
²Department of Physics, Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126 Blindern, N-0318 Oslo, Norway.
³Department of Materials Science, National Research Nuclear University “MEPhI”, 31 Kashirskoe sh, Moscow, Russian Federation
⁴Department of Materials Science & Engineering, Michigan Technological University, USA

Corresponding authors: *jevanthinath.chem@mkuniversity.org, #pearce@mtu.edu

Abstract

Novel aluminum and indium doped zinc oxide (ZnO) bilayer transparent conducting oxide thin films was fabricated by simple sol-gel spin coating method and post-annealed at 500 °C for an hour under nitrogen ambient towards solar cell applications. The structural, electrical and optical properties of both the as-deposited and annealed bilayer thin films were characterized. X-ray diffraction studies show hexagonal wurtzite-type structure of ZnO with (002) orientation, which enhanced with annealing. In atomic force microscopy studies, minimum surface roughness was attained for Al-doped ZnO (AZO)/In-doped ZnO (IZO) bilayer TCO film compared to IZO/AZO bilayer film. The AZO/IZO film sheet resistance improved to 0.057 M ohm/square after post-annealing, while the single layer AZO film sheet resistance degraded upon annealing in nitrogen atmosphere. All the films had an average transmittance in the visible region over 96%.

Key words: Al doped ZnO (AZO), In doped ZnO (IZO), Sol-gel spin coating, electrical and optical properties, bilayer films.
I. INTRODUCTION

Transparent conducting oxides (TCOs) have been widely used for various kinds of optical and electrical device applications due to their excellent combined electrical conductivity and optical transparency in the visible range of the electromagnetic spectrum [1]. Currently, different types of TCO structures such as TCO/Metal/TCO and TCO/TCO have been proposed to enhance the TCO properties towards solar photovoltaic (PV) applications [2, 3]. The dominant TCO is tin doped indium oxide (ITO) as it shows superior electrical resistivity and good transmittance in the visible range [4]. However, indium ore extraction is a challenge and increasing supply demand has led to a rise in costs of this material every year [5]. To overcome the costs, there is a need to find an inexpensive material as a replacement for ITO. Among different TCO materials, zinc oxide (ZnO) has excellent electrical, optical, mechanical, and chemical sensing properties, as well as thermal stability. In addition, more widespread availability in earth (and associated lower costs of the material) allow ZnO to be used in wide range of applications such as gas sensors, catalysis, liquid crystal display, light emitting diodes, electronics, solar PV cells, and transparent electrodes [5, 6]. Importantly, the heterojunction of p-type cuprous oxide (p-Cu$_2$O) with ZnO formed by AZO/ZnO/Cu$_2$O hetero-structure is considered as one of the next generation solar cells [7, 8]. Aluminium doped ZnO (AZO) and indium doped ZnO (IZO) films are attractive candidates in the opto-electronic industry due to their excellent electrical and optical properties [7, 8] and have attracted attention to replace the ITO films with low cost [9, 10]. AZO has attained high thermal stability, lowest sheet resistance, highest optical transmission, while the chemical sensitivity and mechanical properties are similar to the ITO [9, 11]. Zhao et al. prepared the AZO films by spin coating method and annealed using forming gas (10% H$_2$: 90% N$_2$) ambient, they achieved necessary electrical and optical properties for solar cell applications [12]. Likewise, IZO thin films exhibit superior electrical conductivity and optical transmission in the visible region and is widely used for device applications [13]. Hence AZO and IZO thin films have become the most attractive materials in the past decades [14, 15]. In addition, modulation doping in multilayers could improve the sheet resistivity by enhancing the carrier mobility and also exhibit superior anti-reflection properties [2]. The present work focuses on developing monolithic bilayer films with enhanced electrical and optical properties to substitute the ITO films.

II. EXPERIMENTAL

The AZO and IZO layers were prepared by sol-gel process using zinc acetate dihydride [Zn(CH$_3$COO)$_2$·2H$_2$O], ethanol, and monoethanolamine as Zn precursor, solvent, and “sol” stabilizer, respectively [9]. Aluminum nitrate [Al(NO$_3$)$_3$·9H$_2$O] and Indium nitrate [In(NO$_3$)$_3$·xH$_2$O] were used as the Al and In dopant precursors. The doping level of aluminum or Indium in ZnO is 1.5 at%. The sol-solution was aged for 24 hours at room temperature before deposition. The AZO (or IZO) precursor solution was spun on the cleaned glass substrate at a rotation speed of 3,000 rpm for 30s in air. The glass substrate with wet precursor films were placed on a hot plate for 10 minutes at 400°C in air to evaporate the solvent and the process of coating and pre-heat treatment is repeated several times to obtain a continuous single layer AZO (or IZO) film. The samples at this stage are considered as as-deposited films. Then, the films...
were post-annealed at 500 °C for an hour under nitrogen ambient. Similar procedures were followed for fabrication of AZO/IZO and IZO/AZO bi-layer films.

III. RESULTS AND DISCUSSIONS

Figure 1 show the X-ray diffraction (XRD) spectra of undoped ZnO, AZO, IZO, AZO/IZO and IZO/AZO films annealed in nitrogen ambient at 500 °C for an hour. The results demonstrate that all the doped ZnO films exhibit expected hexagonal wurtzite structure. In addition, films were highly oriented along the (002) crystallographic orientation and it indicates the preferential growth of doped ZnO films along the crystallographic c-axis on the glass substrate.

A minor higher angle shift was observed for the AZO, AZO/IZO and IZO/AZO films (shown in the Fig.1 B). A similar trend has been reported for AZO films deposited by magnetron sputtering due to substitution of smaller Al$^{3+}$ ions on Zn$^{2+}$ ion sites [16]. However, the IZO showed a lower angle shift and it was ascribed to the change in the ionic radius of Zn$^{2+}$ (0.074 nm) and In$^{3+}$ (0.080 nm) ions [17,18], which would induced tensile or compressive stress at the interface in the AZO/IZO or IZO/AZO bilayer films. As a result, the crystallinity properties of the bi-layer films were modified, with respect to the single layers. The observed diffraction peak positions in AZO single layer films were in good agreement with previously reported results [19]. The full width at half maximum values obtained such as 0.38, 0.37, 0.45, 0.40 and 0.42° for ZnO, AZO, IZO, AZO/IZO and IZO/AZO nanostructures, respectively and the corresponding grain size values estimated using Scherrer equation were presented in Table 1.

Figure 2 portrays the surface topography from atomic force microscopy (AFM) of AZO, IZO, AZO/IZO and IZO/AZO thin films, which were annealed at 500 °C in nitrogen ambient for an hour. The images were scanned at 256 equidistant locations with the scan length of 2.5 µm. From the result, it is observed that the surface roughness (rms) value of the AZO, IZO and AZO/IZO and IZO/AZO films were 4.78, 4.92, 15.58 and 26.19 nm, respectively. The surface roughness increased for the bi-layer TCO film and attributed to the compressive/tensile stress at the interface of the bi-layers. Fig. 2 (c) indicates that the IZO layer was entirely covered by the AZO layer as most of the IZO surface spikes were covered with AZO layer. Similar trends has been observed for the bilayer of ITO/CdO films deposited by electron beam evaporation technique and the roughness of the bilayer depends on the bottom layer thickness and annealing temperature [20]. The highest roughness value was attained for IZO/AZO films as the IZO film, with slightly larger lattice parameter than undoped ZnO were fabricated on AZO film, with slightly smaller lattice parameter than undoped ZnO. The smaller lattice parameter of AZO induces compressive in-plane strain in the IZO film at the interface and thereby causing tensile stress in the IZO film resulting in higher roughness with increasing IZO film thickness. On the contrary, IZO film will induce tensile in-plane strain in the AZO film and hence the decreased roughness and improve the transmission properties. This observation coincides with the X-ray diffraction studies.

The sheet resistance values of ZnO, AZO, IZO, AZO/IZO and IZO/AZO films was measured using four probe technique (See table 2). From the observed values, the minimum sheet resistance was 0.057 M Ω/□ for the AZO/IZO bilayer TCO annealed in nitrogen ambient and the highest value (104.20 M Ω/□) was attained for the as deposited ZnO film. It should be noted that AZO single layer film resistivity increases upon post-annealing, where as the sheet resistivity
decreases for AZO/IZO bilayer film. The optical transmittance spectra for the post-annealed TCO films are shown in Fig.3. All the TCOs films demonstrate more than 96% transmittance in the visible region (400-800 nm) of the electromagnetic spectrum with high optical average transmittance for single layer films compared to bi-layers which could be due to scattering at the interface of the bi-layer films. Duan et al. reported that the oxygen and nitrogen ambient annealed Mg, Al, and Co doped ZnO thin films exhibited high optical transmittance compared to the vacuum annealed films [21]. The sol gel method based AZO films exhibited the lowest resistivity $1.8 \times 10^{-3} \Omega \text{ cm}$ and optical transparency over 90% in the forming gas ambient annealing [13]. In this work, AZO/IZO bilayer structure demonstrated higher optical transmittance and sufficient sheet resistance for solar cell applications. The extrapolation of Tauc plots $-\alpha h\nu^2$ vs $h\nu$ (for direct band gap, not shown here) and the linear region of the graph to the axis, gives the band gap energy of the respective material [22]. The obtained band gap values varied from 3.22 to 3.30 eV and the values depend on the different layers and annealing nature of the TCO films and the results are presented in table. 2. The optical band gap for undoped ZnO films was 3.28 eV, which is in good agreement with previously reported band gap values of undoped ZnO thin films [23]. Increase in carrier concentration will increase the band gap of the semiconducting material due to Burstein-Moss effect. In addition, the strain introduced in the film will modulate the band gap, hence, the films under study exhibit different bandgap values. The highest optical band gap (3.30 eV) was observed for AZO single layer film annealed in nitrogen ambient. Lin et al. reported a blue shift increases with the increment of the Al/Zn ratios and decrease in lattice parameter [9]. On the contrary, an initial blue shift in bandgap for low doping (< 1 at%) and prominent red shift is observed for In doped ZnO films [24]. A similar observation was made for the single layer AZO and IZO films, and bilayers exhibit the average transmittance of both AZO and IZO layers.

IV. CONCLUSION

In summary, novel AZO/IZO and IZO/AZO bilayers TCOs using simple cost-effective sol gel synthesis annealed under nitrogen ambient has been developed towards solar cell applications. From the structural analysis, it is clear that the films were oriented along the (002) crystallographic orientation of hexagonal wurtzite structure. From the AFM results, the minimum surface roughness was obtained for the AZO/IZO bilayers. In the electrical and optical characterization, the minimum sheet resistance $(0.057 \text{ M } \Omega^{-1})$ and highest average transmission (96.80%) was observed for the AZO/IZO bilayer TCO film and also the sheet resistivity in the bi-layer film enhances upon post-annealing in nitrogen ambient. However, hydrogen ambient post-annealing treatment is required to further improve the electrical properties of the bilayer structures to utilize for solar cells application.

REFERENCES


Fig. 1. (a) XRD patterns of ZnO, AZO, IZO, AZO/IZO and IZO/AZO thin films annealed at nitrogen ambient (b) enlarged XRD spectra for single layer and bilayer TCO films
Fig. 2. AFM 3D images 2.5 μm X 2.5 μm for (a) AZO (b) IZO (c) AZO/IZO and (d) IZO/AZO thin films annealed in nitrogen ambient.
Fig. 3. UV-visible transmission spectra for annealed single and bilayer TCO films
Table 1. Structural parameters of post-annealed ZnO, AZO, IZO and AZO/IZO and IZO/AZO TCO films

<table>
<thead>
<tr>
<th>Sample</th>
<th>d Spacing (Å)</th>
<th>Lattice Constant (Å)</th>
<th>Grain size (nm)</th>
<th>Micro Strain (ε)</th>
<th>Net Lattice Distortion</th>
</tr>
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<tr>
<td>ZnO</td>
<td>2.605</td>
<td>5.210</td>
<td>22</td>
<td>0.090</td>
<td>0.0010</td>
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<tr>
<td>AZO</td>
<td>2.603</td>
<td>5.205</td>
<td>23</td>
<td>0.087</td>
<td>-0.0006</td>
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<tr>
<td>IZO</td>
<td>2.609</td>
<td>5.217</td>
<td>19</td>
<td>0.107</td>
<td>0.0023</td>
</tr>
<tr>
<td>AZO/IZO</td>
<td>2.604</td>
<td>5.208</td>
<td>21</td>
<td>0.096</td>
<td>0.0005</td>
</tr>
<tr>
<td>IZO/AZO</td>
<td>2.604</td>
<td>5.208</td>
<td>20</td>
<td>0.099</td>
<td>0.0005</td>
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</table>

Table 2. Resistivity and optical properties of as-prepared and annealed ZnO, AZO, IZO and AZO/IZO and IZO/AZO TCO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Transmittance (%) (400-800 nm)</th>
<th>Optical Band Gap (E_g) in eV</th>
<th>Sheet Resistance M Ω/Square</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>As deposited</td>
<td>Annealed</td>
<td>As deposited</td>
</tr>
<tr>
<td>ZnO</td>
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<td>97.49</td>
<td>3.28</td>
</tr>
<tr>
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<td>97.79</td>
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<tr>
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<tr>
<td>AZO/IZO</td>
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<td>96.80</td>
<td>3.25</td>
</tr>
<tr>
<td>IZO/AZO</td>
<td>97.10</td>
<td>96.22</td>
<td>3.22</td>
</tr>
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