EFFECTS OF TARGET COMPOSITION ON THE OPTICAL CONSTANTS OF DC SPUTTERED ZNO:AL THIN FILMS

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ABSTRACT
Al doped ZnO thin films were deposited from ZnO:Al ceramic and Zn:Al metal alloy targets in Ar and Ar + O₂ atmospheres respectively, using Direct Current (DC) magnetron sputtering. The samples exhibited transmittance T > 80% in visible region with good NIR shielding. The results indicated that, band gap energy ranged from 3.34 to 3.44 eV and 3.39 to 3.46 eV for films prepared from alloy and ceramic targets, respectively. Films obtained from alloy target at a substrate temperature of 200 °C showed low electrical sheet resistance of 10 Ω/sq, and highest values of mobility (15.9 cm²/Vs) and carrier concentration (2.98 × 10²¹ cm⁻³). However, films prepared from ceramic target at a substrate temperature of 300 °C revealed the highest sheet resistance of 32 Ω/sq, with lower values of mobility (14.1 cm²/Vs) and carrier concentration (1.92 × 10²⁰ cm⁻³). The increase in sheet resistance and decrease in mobility as well as carrier concentration might be due to increased scattering centers for carriers, resulting to increased sheet resistance. Optical spectra of the films were fitted to SCOUT software in order to determine the refractive index, n and extinction coefficient, k. Generally, the calculated n and k in the visible part of the solar spectrum for different samples, ranged from 1.59 to 2.2 and 0.00013 to 0.0194 respectively, which are in agreement with results obtained using other methods. In general, the findings of this study shows that alloy target is suitable for deposition of ZnO:Al thin films for devices/applications where low deposition temperature is required.

Key words: DC Magnetron Sputtering, Optical Constants, Transparent Conducting Oxides (TCO)

1.0. INTRODUCTION
Al doped zinc oxide films (ZnO:Al) are wide-band-gap semiconductors with high visible transparency, high reflectance in the near infrared (NIR) wavelength along with good electrical conductivity of nearly semi-metallic regime. The combination of high visible transparency with good electrical conductivity makes ZnO:Al films widely applicable for potential application in optoelectronic devices where either optical, or electrical properties or both are used (Minami et al. 1985, Schaefer 1997, Granqvist 2007, Li et al. 2012). However, ZnO:Al properties are highly dependent on defect structure, deposition technique and the deposition parameters employed. Film thickness and substrates used can also have great influence...
on the properties (Sittinger et al. 2010, Reddy et al. 2012).

ZnO:Al films has recently gained much attention as a promising alternative material to tin oxide (SnO$_2$), indium oxide (In$_2$O$_3$) and indium- or fluorine-doped SnO$_2$ because of its competitive electrical and optical properties as well as availability in natural resource as being a low-cost material (Kim et al. 2007, Ehrmann and Reineke-Koch 2010, Kuo et al. 2012). Apart from that, ZnO has good chemical stability in hydrogen plasma, for example in silane (SiH$_4$) which is used for the preparation of a-Si:H thin film solar cells (Beyer et al. 2007, Huang et al. 2011). Moreover, it has been reported that ZnO:Al films have good roughening and surface texturing which helps to enhance light scattering and absorption inside a solar cell and thus enhance the performance of a solar cell (Beyer 2007).

Various deposition techniques have been employed in preparing ZnO:Al films. Besides chemical vapour deposition (CVD), spray pyrolysis, pulsed laser deposition and sol-gel, magnetron sputtering is widely used (Wang et al. 2009, Fernández and Naranjo 2010, Sittinger et al., 2010, Hwang et al. 2011, Alnajjar 2012). This technique allows deposition of ZnO:Al films at low substrate temperatures down to room temperature and at high deposition rates. The sputtered films show good adhesion on substrates and the technique offers very good thickness uniformity and high density of the films (Hwang et al. 2011, Alnajjar 2012). Taking this into account, magnetron sputtering is considered as a favourable deposition technique in which ZnO:Al films with good optical properties can be deposited.

Among the factors that influence physical properties of DC sputtered ZnO:Al thin films are the target composition and deposition parameters used. It was reported that, using metallic Zn:Al targets in preparing sputtered ZnO:Al resulted in high quality films with good physical properties (May et al. 2003, Hong et al. 2003, Suchea et al. 2007, Sitnesser 2009). Other literatures, (Wang 2009, Huang et al. 2011) reported that high quality ZnO:Al thin films with good physical properties were obtained by preparing the films from ceramic targets. In the present work, investigations on the effect of target composition (ceramic against metallic targets) on the optical constant of ZnO:Al thin films have been carried in order to identify the suitable type of target for the preparation of good DC sputtered ZnO:Al thin films for solar cell applications.

2. MATERIALS AND METHODS
2.1. SAMPLE PREPARATION
ZnO:Al films were deposited on soda lime glass (SLG) substrates by reactive DC magnetron sputtering using BALZER BAE 250 coating unit. DC magnetron sputtering using metallic targets consisting of a Zn:Al alloy (2% Al) and ceramic target containing ZnO:Al (2% Al) (both from AJA International Inc., USA) were employed. The sputtering chamber was pumped down to a base pressure of 4.3 × 10$^{-6}$ mbar using a turbo-molecular pump backed by a rotary pump. The sputtering gas (Ar 99.999%) and reactive gas (O$_2$ 99.999% purity) were introduced into the chamber separately, and were controlled through the gas mass flow rate controllers. The gas flow rates were controlled precisely to allow flow rates of oxygen and argon gases at about 5.0 – 5.5 and 60 ml/min, respectively for the case of Zn:Al target. However, for ceramic target ZnO:Al oxygen and argon gases flow rates were at about 0 ml/min and 10 – 70 ml/min, respectively. The substrate temperature was varied from 100 °C to 350 °C, however, in this study, the optimal values of substrate
temperatures were 200 °C and 300 °C for films prepared from alloy and ceramic targets, respectively. The sputtering power of 70 W was used and pre-sputtering for 10 minutes was made so as to make the plasma stable and Target to substrate distance was fixed at 15 cm for both targets.

2.2. CHARACTERIZATION TECHNIQUES

The computerized, high sensitivity surface profiler, Alpha step IQ Surface profiler was used to measure the thickness of ZnO:Al films. A small portion at the edge of the substrate was covered using adhesive Teflon tape before deposition so as to create a step for measuring the film thickness. X-ray diffractometer with $\theta - 2\theta$ scanning mode was used for crystalline characterization. The diffraction angle ($2\theta$) was varied from 5.000° to 84.997°. The electrical properties were investigated using a Hall Effect Measurement System (Ecopia HMS 3000) connected to the computer for displaying electrical properties. The optical transmittance and reflectance in the UV/VIS/NIR was measured in the wavelength range of 250 - 3000 nm at an interval of 1 nm by using Shimadzu SolidSpec-3700 DUV Spectrophotometer.

Optical spectra of the films were fitted to SCOUT software (Theiss 2008) in order to determine the refractive index, $n$ and extinction coefficient, $k$, whereby three layers; air, ZnO:Al and substrate were theoretically implemented. The classical Drude model was used in which the fundamental quantity describing the dielectric response of any material is the complex dielectric constant related to the complex refractive index as shown by equation 1.

$$\tilde{n} = n(\lambda) + ik(\lambda) = \sqrt{\varepsilon_{re} + i\varepsilon_{im}}$$  \hspace{1cm} (1)

where $\tilde{n}$ is the complex refractive index, $n(\lambda)$ refractive index and $k(\lambda)$ extinction coefficient. The real ($\varepsilon_{re}$) and imaginary parts ($i\varepsilon_{im}$) of the dielectric function are related to the optical constants ($n$ and $k$) by equation 2 and 3 (Hamberg and Granqvist, 1986);

$$\varepsilon_{re} = n^2 - k^2 = \varepsilon_{\infty} \left( 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \right)$$  \hspace{1cm} (2)

$$\varepsilon_{im} = 2nk = \varepsilon_{\infty} \frac{\Gamma}{\omega} \left( \frac{\omega_p^2}{\omega^2 + \Gamma^2} \right)$$  \hspace{1cm} (3)

Where $\omega_p$ is the plasma frequency, $\Gamma$ is the damping constant and $\varepsilon_{\infty}$ is the high frequency dielectric constant.

3.0. RESULTS AND DISCUSSION

3.1. STRUCTURAL CHARACTERIZATION

The crystalline structure and orientation of the ZnO:Al films having thickness of 300 nm were investigated by XRD. Figure 1 shows the XRD pattern of ZnO:Al thin films deposited at a substrate temperature of 200 °C for alloy target and 300 °C for ceramic target, where the oxygen and argon flow rate were kept at 5.17, 5.19 and 5.23 ml/min and 20, 30, 50 ml/min, respectively. The films exhibited a high degree of preferred orientation, which depends on the various gas flow rates. In this study, all prepared ZnO:Al films exhibit strong diffraction peaks of (002) which is consistent with hexagonal wurzite phase of ZnO. For the films prepared using alloy target, increasing oxygen flow rate from 5.17 ml/min to 5.19 did not change the locations of the measured diffraction peaks but they become more intense. However, further increase in oxygen flow rate to 5.21 ml/min, the intensity of
the peak decreases. For films prepared from ceramic target, it is seen that the peak becomes more intense and sharper with decreasing argon flow rate. This means that the film crystallinity is improved and the grain size of the crystallites becomes larger at a lower argon flow rate. In this study, lower gas flow rate are expected to improve the crystallinity of the film by increasing the moment transfer of sputtered atoms to the film growing on the heated substrate.

A weak diffraction peak of (201) was observed in films prepared using ceramic and alloy targets at an Ar and oxygen flow rate of 30 ml/min and 5.23 ml/min, respectively, which then disappeared with decrease in Ar flow rate. The diffraction peaks of (100) and (004) were also observed in both films but neither aluminium oxide (Al₂O₃) nor metallic (Zn or Al) phases were observed. This indicates that, the prepared ZnO:Al films were crystalline exhibit a strong c-axis preferred orientation.

### 3.2 ELECTRICAL PROPERTIES

A comparative films study prepared from ceramic target having resistivity and mobility ranging from $3.421 \times 10^{-3}$ to $4.023 \times 10^{-4} \ \Omega cm$ and 14.08 to 16.53 cm²/Vs, respectively, the electrical properties of films prepared using alloy target are effectively improved. The films exhibit relatively low resistivity ranging from $(1.588 – 2.908) \times 10^{-4} \ \Omega cm$ which is close to those reported elsewhere (Minami et al. 1985) and higher mobility ranging from 13.5 to 16 cm²/Vs. The carrier concentration for films prepared from alloy target ranged from $1.532 \times 10^{21}$ cm⁻³ to $1.981 \times 10^{21}$ cm⁻³ while those prepared from ceramic target ranged from $3.08 \times 10^{20}$ cm⁻³ to $1.33 \times 10^{21}$ cm⁻³.

Despite the fact that both films having the same thickness ~300 nm but they have quite different electrical properties as show in Table 1. The good electrical properties of the films prepared from alloy target might be due to the incorporation of Al from the alloy target into zinc in the lattice and thus increasing carrier concentration and mobility of the films. However, with increasing oxygen gas flow into the chamber, lead to the increase in resistivity and decrease mobility and carrier concentration. This observed increase in resistivity with increase in oxygen gas flow rate can be caused by increased oxygen (O) atoms involved in the process of reactive sputtering, oxygen atom combined to metal oxide with metal, leading to the decreased Zn interstitial...
atoms. Furthermore, metallic Al atoms might be combined with oxygen atoms to oxides, and thus increasing resistivity and then after decrease in mobility and carrier concentration. Similar results were reported by Liu et al. (2010).

The same trend was also observed for films prepared using ceramic target, where the resistivity was found to decrease with the decrease of argon gas flow rate. The lowest resistivity of $4.023 \times 10^{-4}$ was obtained at an argon gas flow rate of 20 ml/min. The conduction mechanism of ZnO:Al films prepared using ceramic target, is affected by argon flow rate. This is due to the variation in grain size, which differs accordingly with argon flow rate (Dong-Joo et al. 2004). In this study, the mobility and carrier concentration were found to decrease with increase in argon gas flow rate due to the fact that at increased argon flow rate resulted in stronger collision between the sputtered target atoms with the argon atoms thus reducing kinetic energy of the sputtered atoms. This can hinder their migrating capability on the substrate, resulting in small grain size of the film which also can reduce the mobility of the film. Collectively (from Table 1), the films grown from the alloy targets exhibited much preferable electrical characteristics, whereas lower sheet resistance and resistivity and higher mobility and carrier concentration have been obtained at a substrate temperature of 200 °C. This demonstrates that DC sputtering from alloy target is better suited for TCO since it can be easily obtained at low temperature with good electrical properties.

### Table 1: Properties of notable ZnO:Al films prepared from alloy and ceramic targets, at substrate temperature of 200 °C and 300 °C, respectively, at a sputtering power of 70 W. Thickness of both films was ~300 nm.

<table>
<thead>
<tr>
<th>Properties</th>
<th>$O_2$ (ml/min)</th>
<th>$R_s$ Ω/sq</th>
<th>$\rho \times 10^{-4}$ Ωcm</th>
<th>$\eta \times 10^{21}$ cm$^{-3}$</th>
<th>$\mu$ cm$^2$/Vs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Zn:Al) target</td>
<td>5.15</td>
<td>19.3</td>
<td>3.931</td>
<td>1.75</td>
<td>15.04</td>
</tr>
<tr>
<td></td>
<td>5.17</td>
<td>14.11</td>
<td>2.204</td>
<td>1.98</td>
<td>15.80</td>
</tr>
<tr>
<td></td>
<td>5.19</td>
<td>10.8</td>
<td>2.307</td>
<td>2.98</td>
<td>15.97</td>
</tr>
<tr>
<td></td>
<td>5.21</td>
<td>15.2</td>
<td>2.248</td>
<td>1.92</td>
<td>15.17</td>
</tr>
<tr>
<td></td>
<td>5.23</td>
<td>17.5</td>
<td>2.523</td>
<td>1.93</td>
<td>15.03</td>
</tr>
<tr>
<td><strong>Ceramic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ZnO:Al) target</td>
<td>10</td>
<td>46.3</td>
<td>0.974</td>
<td>0.87</td>
<td>14.01</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>30.7</td>
<td>4.023</td>
<td>0.92</td>
<td>14.18</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>34.5</td>
<td>9.625</td>
<td>0.90</td>
<td>14.06</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>38.1</td>
<td>9.801</td>
<td>0.89</td>
<td>13.73</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>45.3</td>
<td>0.723</td>
<td>0.86</td>
<td>13.47</td>
</tr>
</tbody>
</table>

The optical properties were controlled by adjusting Ar gas flow ratio and oxygen flow rate as a mixture of Ar+O$_2$ gases for ceramic and alloy targets, respectively. The transmittance of the films prepared from both targets was higher than 80 % with oscillatory character due to interference effects in the visible region from 300 to 800 nm with a sharp fall in the transmittance at the absorption edge as shown in panels a and b of Figure 2. Plasma frequency shifted to higher wavelength with increase in oxygen flow rate in the mixture of Ar+O$_2$ gases and Ar flow ratio for films prepared from alloy and ceramic targets, respectively, and showed excellent NIR shielding as can be seen in Figure 2. This might be due to zinc adsorption and substitutional doping of an Al$^{3+}$ at the Zn$^{2+}$ site creating one extra free carrier in the process.
which occurs at a substrate at low gas flow ratios which leads to the increase in carrier concentration (Sittinger et al. 2009, Sittinger et al. 2010, Hwang et al. 2011). An increased carrier concentration can give increased absorption in the long wavelength region due to free electron gas. Similar results for the films prepared using alloy target were reported elsewhere (Theiss 2008, Liu et al 2010, Sittinger et al. 2010, Hwang et al. 2011). The films from both targets show typical optical characteristics of TCOs whereas they have a transmission window in the 400 – 1500 nm wavelength range. However, the highest average optical transmittance was achieved using ceramic target and was calculated to be ~80.14 %. The difference arises in near normal reflectance in the NIR region where the films prepared from alloy target showed high NIR reflectance, higher than 80%. The optical energy gap is determined from transmittance spectral data using Equation 4, which relates the absorption coefficient ($\alpha$) and the gap energy ($E_g$).

$$a\nu = B(\nu - E_g)^{1/2}$$

where $\nu$ is the photon energy, $E_g$ is the optical gap energy for direct allowed transitions and $B$ is the factor depends on the transition probability and is taken as constant within the optical frequency range. The band gap was observed to shift from 3.49 to 3.43 eV with decrease in argon gas flow rate. Films prepared from alloy target the band gap was increased from 3.34 to 3.54 eV with decrease in oxygen gas flow rate. This is possibly due to the Burstein-Moss shift which is attributed to an increase in the carrier concentration as it is seen section 3.2. This increase in carrier concentration blocks the lowest states (filled states) in the conduction band from absorbing the photons (Liu et al 2010).

Figure 2. (a) Optical transmittance and reflectance spectra of ZnO:Al films grown at various O$_2$ flow ratio as a mixture of Ar + O$_2$ gas at 200 °C (b) Optical transmittance and reflectance spectra of of ZnO:Al thin films prepared at different argon gas flow rate.
resulting in widening of the band gap energy. The shift in absorption edge might also be due to the presence of residual compressive stress as reported by Özgür and his co-workers (Özgür et al. 2005). The kinks observed at wavelength 870 nm were due to default switching of the detectors of the Spectrophotometer.

The optical constants (refractive index, \( n \) and extinction coefficient, \( k \)) as obtained by fitting the experimental spectral transmittance data using SCOUT software corroborate with the results of polycrystalline ZnO:Al thin films calculated by other methods indicating excellent fit of the models used. As can be seen from (Figure 3), with variation of the oxygen gas flow rate the refractive index varies as well as the extinction coefficient but in a less pronounced way. It was with the increase of the oxygen flow rate, ZnO:Al thin films tend to be non-stoichiometric and the packing density increases which results in an increase of the refractive index (Jung et al. 2003, Al-Hardan et al. 2010). The well known that the refractive index is closely related to the density of materials, being lower at lower density. Furthermore, the number of oxygen atoms may be more than the number of zinc atoms and the film tends again to be non-stoichiometrical which exhibited a lower degree of crystallinity as depicted shown in Figure 1, which results in an increase of the refractive index (Jung et al. 2003). Similar results were observed for films prepared from ceramic target, refractive indices were found to increase with the increase of argon gas flow ratio as shown in Figure 4. The reason behind the decrease can be attached to the increase in carrier density, which results in the shift of both plasma frequency and the band gap to higher energies, similar to that reported for ITO films (Qiao et al. 2006).

In the visible region, refractive index \( n \) decreases with wavelength, which correlates with the corresponding increase in transmittance. The obtained values of \( n \) agree well with the values obtained using other methods reported elsewhere (Bandyopadhyay et al. 2002, Jung et al. 2003, Xue et al. 2006, Li et al 2008, Li-Ping et al. 2012). This is a typical behavior for a semiconductor and thus shows a normal dispersion. The extinction coefficient \( k \) as a function of wavelength of the films is almost constant in the visible region for all the samples indicating weak absorption as evidenced by high transmittance in this region. These films exhibit

**Figure 3.** Dependence of refractive indices and extinction coefficients of ZnO:Al films on O\(_2\) flow rates.

**Figure 4.** Dependence of refractive indices and extinction coefficients of ZnO:Al films on argon flow rates.
high extinction coefficient in the plasma edge, suggesting absorption of photons in NIR regions, respectively. However, for both films, the change was small implying little absorption in the visible range, which is consistent with the transmittance spectra results, as shown in Figure 2(a and b). The result is in agreement with those reported for ZnO:In (Li-Ping et al. 2012).

4.0. CONCLUSION

In the present work ZnO:Al thin films were deposited onto soda lime glass (SGL) slides by reactive and non-reactive DC magnetron sputtering. The effects of target composition (Zn:Al (2% Al) metal alloy and ZnO:Al (2% Al) ceramic targets on optical constants of ZnO:Al thin films were studied. XRD pattern of ZnO:Al films were largely grown along (002) reflection plane under lower oxygen and argon gas flow rate. The deposited ZnO:Al films were highly conductive. However, films with lowest electrical resistivity of $2.04 \times 10^{-4}$ and highest carrier concentration and mobility of $2.98 \times 10^{21}$ cm$^{-3}$ and 15.97 cm$^2$/Vs, respectively, were obtained from ZnO:Al films prepared from alloy target. All the films showed more than 80% transparency in the entire visible region. The values of $n$ and $k$ were found to vary significantly with deposition parameters, whereby for different samples ranged from 1.59 to 2.2 and 0.00013 to 1.2194 respectively. Nevertheless, the obtained values are in range of the values reported for ZnO:Al films. Despite similar optical constants and being in range with those reported in literatures, these results confirm that the films with good optical properties can be achieved using metal alloy target, since good electrical together with structural properties were obtained using metal alloy target. This demonstrate that ZnO:Al thin films prepared from metal alloy can be used as an appropriate TCO material in CIGS solar cells since they are deposited at lower temperature 200 °C recommended for CIGS solar cells.

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