Correlation between the electrical and structural properties of aluminium-doped ZnO thin films obtained by direct current magnetron sputtering

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Abstract. High quality Aluminium-doped Zinc Oxide (AZO) films have been obtained by suitably controlling the magnetron sputtering parameters and the substrate temperature. The X-ray diffraction studies showed that a transition of orientation from (002) plane to (103) plane, versus substrate temperature. The surface morphology characterized by scanning electron microscopy and atomic force microscopy exhibited a dense and compact structure at higher temperature. For 200 nm thick AZO films deposited at temperature 530°C, using a ZnO target with an Al\textsubscript{2}O\textsubscript{3} content of 3 wt\%, the lowest electrical resistivity is $6.8\times10^{-4}$ $\Omega\cdot$cm and transmittance is over 85% in the visible spectral region. The conductivity improvement of AZO films was closely related to the crystallinity characterized by the (103) orientation and the densely packed structure.

1. Introduction

For the next generation flat panel displays, solar cells, organic light emitting diodes and other optoelectronic devices, transparent conducting oxide (TCO) films have a wide range of applications as transparent electrodes [1-2]. Aluminium-doped zinc oxide (AZO) has attracted much attention because of its good electrical properties with high optical transparency comparable to indium tin oxide (ITO) [3-4]. Moreover, this oxide is abundant, non-toxic, easily fabricated at industrial scale and cheap, compared to ITO, which are the reasons that stimulating the research on In-free electrodes. AZO have been deposited by many methods including sputtering [5], pulsed laser deposition [6] and evaporation [7]. Among the deposition techniques, magnetron sputtering technique has been widely used because of its high deposition rate and high stability for large area films. The most of results in literature agrees with the preferred growth orientation for AZO thin films, which is along the (002) direction at low and high deposition temperature [8-10]. We rather focus on the improvement in the electrical properties when the growth orientation changes from (002) to (103) plane with increasing substrate temperature. We will explain the relationship between the (103) orientation and the electrical properties.

In this paper, AZO films were deposited by DC magnetron sputtering with different substrate temperatures. Structural, electrical and optical properties of AZO thin films were analysed in order to optimise its TCO properties for its application on Cu(InGa)Se\textsubscript{2} based solar cells fabricated on metal coil in a continue line process.
2. Experimental Procedures

(AZO) films have been prepared on soda-lime glass substrate by DC magnetron sputtering technique. A target with a mass proportion ZnO and Al\(_2\)O\(_3\) (97:03), (99.95% purity), a size of 76.2 mm in diameter and 6 mm in thickness has been employed as source material. Initially, the chamber was evacuated to a pressure of \(5 \times 10^{-6}\) Torr by a turbo-molecular pump and Ar gas was used as a sputtering gas. The substrates were degreased in acetone, rinsed in de-ionized water followed by rinsing in ethanol and then dried under N\(_2\) gas flow, before introducing into the sputtering chamber. The target to substrate distance is 170 mm and the sputter power is kept at 120 W for all depositions. The AZO target surface was pre-sputtered for 5 minutes in order to remove contaminations before deposition. Substrate temperature \(T_s\) was varied from 25 to 530°C and working pressure has been kept at of 3 mTorr during sputtering process. The thickness of all AZO films was around 200 nm, as-confirmed by a Veeco Dektak surface profilometer.

The structural properties of AZO films were characterized by a grazing angle X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometer) with Cu K\(_\alpha\) radiation (\(\lambda = 0.15406\) nm) at fixed incidence angle of 2°. The surface morphology of the films was observed by scanning electron microscopy (SEM) (JEOL 7500F Company). The topography and surface roughness of the samples were studied by atomic force microscopy (AFM) with a commercial microscopy (Nanoscope IIIa, Digital Instruments) operating in tapping mode (TM), using a standard silicon cantilevers with spring constant \(\sim 42 \text{ N.m}^{-1}\) and 369 kHz driving frequency. All images were recorded in ambient air at a scan frequency of 1-1.5 Hz. The background slope due to piezoelectric non-linearity was corrected using first or second orders polynomial functions. The electrical resistivity was measured by the four probe method and the optical transmittance of AZO films was measured by a Perkin-Elmer UV-visible spectrophotometer in the range 250 – 2000 nm.

3. Results

3.1. Structural properties

The crystalline structure and orientation of the AZO thin films have been examined by X-ray diffraction (Figure 1). No Al\(_2\)O\(_3\) phase has been evidenced in the XRD patterns, which implies that Al atoms are substituted in the ZnO hexagonal lattice or segregated to the nanocrystalline region in grain boundary [11]. The XRD patterns show that the AZO films deposited at room temperature are described by a strong peak at \(2\theta = 34.43^\circ\) and a weaker peak at \(2\theta = 62.88^\circ\). These reflections were identified respectively as (002) and (103) plane of hexagonal wurzite ZnO [12], in which a preferred orientation along the c-axis is observed. However, when the substrate temperature rises, a clear crystallographic orientation change of AZO films is observed. For high deposition temperature, the intensity of (103) diffraction peak increases while intensity of (002) peak decreased. A transition of the growth mode from (002) vertical to (103) lateral growth is clearly observed due to the crystalline evolution during the deposition at high substrate temperature. Although such orientation change is rarely seen in the literature compared to (002) growth, Huang et al. [13] have also observed the (103) orientation change but with different deposition condition such as working pressure, oxygen content and film thickness.

| \(T_s\) (°C) | \(\rho\) (\(\Omega\).cm) | \(T_{\text{aver}}\) (%) | \(E_g\) (eV) | Crystallite size (nm) |
|-----------|-----------------|-----------------|-----------|-----------------|
| 25        | \(1.7 \times 10^1\) | 93              | 3.25      | 11.8            |
| 375       | \(1.1 \times 10^2\) | 86              | 3.39      | 18.8            |
| 455       | \(1.7 \times 10^3\) | 86              | 3.48      | 17.9            |
| 530       | \(6.8 \times 10^4\) | 85              | 3.55      | 17.2            |

The crystallite size may be estimated from the full-width at half maximum (FWHM) of the high intensity peak (002 or 103 orientation) by Scherrer equation [14]:
where $\lambda$, $\theta$ and $B$ are the X-ray wavelength, Bragg diffraction angle and FWHM ($\theta$ in radian) of the (002) reflections, respectively. For sputtered AZO films, this gives an estimated grain size in the range 16-20 nm (Table 1).

$$D = \frac{0.9\lambda}{B\cos\theta}$$  \hspace{1cm} (1)

![Figure 1. XRD patterns of ZnO:Al films deposited at different substrate temperatures](image)

The AZO surface morphology characterized by SEM and AFM are shown in Figures 2(a) and 2(b). The grain size increases with the substrate temperature. At room temperature, the grains are uniform with repetition and exhibit a distinct grain boundary structure. At 375°C, the films show a textured surface and consist of tapered crystallites separated by voids. Surface morphology and the grain size are strongly influenced by the deposition temperature.

![Figure 2. SEM micrographs of AZO films deposited by DC magnetron sputtering at different substrate temperatures: (a) 25°C, (b) 375°C, (c) 455°C and (d) 530°C.](image)
When the substrate temperature increases from 375°C, grain coalescence is observed as shown in Figures 2(c) and 2(d). Corresponding situation in XRD above this temperature is change in preferential orientation and above this temperature the grain size also does not grow (Table 1) [15]. Due to this grain coalescence, an aggregate structure is formed and the films consist of a dense array of grains without discernible boundaries are observed [16-17]. Hence the higher substrate temperature may give more tightly packed grains with an orientation change in our study.

AFM images of the AZO films confirm the SEM results. Figures 3(b) and 3(c) show the grain coalescence when compared to the well distinct grains (Figure 3(a)). With increasing deposition temperature, a decrease in surface roughness (Figures 3) is observed and this implies the textured surface. The root-mean-square (RMS) surface roughness is $\text{RMS} = 7.6 \text{ nm}$ for $T_s = 375^\circ \text{C}$ and $\text{RMS} = 4 \text{ nm}$ for $T_s = 530^\circ \text{C}$, indicating a smooth surface and low roughness of AZO films.

3.2. Electrical properties

As shown in Figure 4, the resistivity of AZO films decreases sharply from $1.7 \times 10^{1}$ to $6.8 \times 10^{-4}$ $\Omega \cdot \text{cm}$ when the deposition temperature ranges from 25 to 530°C. That corresponds to the typical range one can find in the literature [18-19]. The lower value of electrical resistivity occurs with orientation change from (002) to (103) in the XRD patterns, while high resistivity is attributed to the (002) diffraction peak.

3.3. Optical properties

Figure 5(a) shows the optical transmittance of 200 nm AZO films prepared at different substrate temperatures, constant working pressure, $P_{\text{working}} = 3$ mTorr and discharge power, $P_{\text{DC}} = 120$ W. The average optical transmittance in the visible range is more 85% for all samples [20-21]. As the deposition temperature increases, the optical absorption edge blue shifts monotonically. This trend is well known and explained by the increase in carrier concentration stated by the Burstein-Moss
effect [22-23]. The decrease in transmittance in the long wavelength region is due to the reflection by the collective oscillation of conduction band electrons [24]. Hence this is attributed to the increasing carrier concentration with substrate temperature. For the direct optical gap semiconductor, \( \alpha \) and the optical band gap, \( E_g \), are related by [25]:

\[
\alpha = (h \nu - E_g)^{1/2}
\]

(2)

where \( h \) is Planck’s constant, and \( \nu \) is the frequency of the incident photon. Figure 5(b) shows the plot of \( \alpha^2 \) vs \( h \nu \). ZnO is the direct band gap semiconductor, so the x-axis intercept of the linear extrapolation of the curve plotted between \( \alpha^2 \) and \( h \nu \) will directly give the band gap (\( \alpha^2 = 0 \)). From Figure 5(b), \( E_{g0} \) for the pure ZnO film is \( E_{g0} \approx 3.3 \) eV and the \( E_g \) for samples prepared at room temperature is \( E_g \approx 3.25 \) eV. When the substrate temperature increases, the \( E_g \) rises until \( 3.55 \) eV at \( T_s = 530^\circ\)C. These results are consistent with the results obtained from literature [26-27].

![Figure 5](image-url)

**Figure 5.** (a) Optical transmittance of AZO thin films prepared at different substrate temperatures and (b) square of the absorption coefficient as a function of photon energy.

### 4. Discussion

When the substrate temperature is over \( 375^\circ\)C, the morphology of AZO films is an aggregate structure due to grain coalescence [16-17]. The higher substrate temperature gives more tightly packed grains. The electrical resistivity is improved, due to the grain coalescence structure and lowest resistivity of \( 7 \times 10^{-4} \) \( \Omega \)cm is obtained. This is mainly attributed to the decreasing of number of scattering centres and trapping centres in the grain boundaries in which the high dense and packed grains cause an increase of carrier mobility and electron concentration [28].

The observed tightly packed grains growth is associated with the strongly marked preferred orientation change from (002) reflection to (103) reflection which is rarely observed. In our study, orientation change is attributed to the rise in substrate temperature and this accompany with grain coalescence. In many works, the minimum resistivity has been related to the presence of the strong (002) reflection in the XRD patterns. Very few have reported this orientation change. For example Gao et al. [29] reported this orientation change while growing films by pulsed DC sputtering. Even though the explanation is not given, there is a close relation between the resistivity of the film and its crystallographic orientation change. Huang et al. [13] rather attribute low resistivity to the better crystallallinity and the larger grain size, even though the same orientation change was observed. But he observes this orientation change, when the working pressure rises up from 0.2 to 0.93 P and no remarkable variation of carrier concentration was observed in his study. Further the film deposited at 0.4 Pa presents lowest sheet resistance and rise up again while (103) peak still grows with working pressure.
In this work, we rather correlate the improvement of the electrical resistivity, not only with the formation of aggregate structure, but also with film growth along with (103) direction. The widening of the band gap is related to the increase of carrier concentration and corresponds to the low electrical resistivity state.

5. Conclusions
Aluminium-doped zinc oxide thin films have been prepared on sodalime glass substrate by DC magnetron sputtering with the ZnO target containing 3 wt% Al₂O₃, at different substrate temperatures. The crystallographic structure of as-prepared AZO films is hexagonal wurzite, in which the films are oriented along the c-axis with a dominant peak (002) in the X-ray diffraction pattern at room substrate temperature, whereas at higher deposition temperature the strongest intensity is associated to the (103) reflection. Moreover, the electrical and optical properties are enhanced at higher deposition temperature. The lowest resistivity of 6.8×10⁻⁴ Ω.cm and transmittance over 85% in the visible spectral region are obtained at Tₛ = 530°C. The SEM and AFM results have shown that the small grains are distributed uniformly at low temperature and grain coalescence occurs at Tₛ > 455°C. The optical energy band gap for AZO films is found to increase with the deposition temperature due to higher carrier concentration.

The highest intensity of (103) diffraction peak leads to the lowest resistivity state, associated to the grain coalescence structure and the high optical band gap. However further studies are going on to bring out exact correlation between the orientation change and lower resistivity.

6. References
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