Improving the structural, optical and electrical properties of Al-doped ZnO thin films: Effects of post-synthesis annealing temperature

W. Cher, S. Yick, S. Xu, Z. J. Han, K. Ostrikov

Abstract

Al-doped ZnO (AZO) thin films were deposited onto glass substrates using radio-frequency (RF) reactive magnetron sputtering and the improvements in their physical properties through post-synthesis thermal treatment were reported. X-ray diffraction spectra show that the structure of films can be controlled by the annealing temperatures, with the best crystallinity obtained at 400 °C under a nitrogen atmosphere. The improved film quality also features better optical transmittance as indicated by UV-Vis spectral measurements. Furthermore, the sheet resistivity is found to decrease from $1.87 \times 10^{-3}$ to $5.63 \times 10^{-4}$ Ω·cm and the carrier mobility increases from 6.47 to 13.43 cm$^2$·V$^{-1}$·s$^{-1}$ at the optimal annealing temperature. Our method demonstrates a simple yet effective way in controlling the structural, optical and electrical properties of AZO films, which is important for the development of high-performance transparent conductive oxide (TCO) materials for numerous applications.
1. Introduction

Transparent conducting oxide (TCO) materials have long been considered as promising functional materials in applications such as flat panel displays [1, 2], thin film solar cells [3-5], and laser and light emitting diodes [6-8], due to their distinctive combination of optical transparency in the visible spectrum and high electrical conductivity [9]. Presently indium tin oxide (ITO) is the most-widely employed material for TCO applications. However, large-scale implementation of ITO is severely hampered due to the scarcity, toxicity and high cost of indium. Alternative TCO materials with comparable device performance to that of ITO are therefore highly desired [10-12]. In the recent development, aluminium-doped zinc oxide (AZO) is considered as one of the best candidates due to several advantages, such as lower cost arising from the abundance of zinc and aluminium, non-toxicity, better optical transmission in the visible spectrum, as well as better structural and photo stability [13].

The fabrication of AZO thin films has been achieved by several methods, including chemical vapour deposition [14], arc physical vapour deposition [15], pulsed laser deposition [16], sol-gel synthesis [17] and magnetron sputtering [3, 18]. In attempting to make AZO a cost-efficient substitute to ITO with comparable device performance, many efforts have been spent to improve the film quality through optimizing the processing parameters (e.g., substrate heating, pressure, bias, power, etc.) during the fabrication [19, 20]. In contrast to that, here we demonstrate that the film quality of as-deposited AZO can be effectively controlled by post-synthesis thermal treatment and the best film crystallinity is obtained at 400 °C under a nitrogen atmosphere. We also show that the improved film crystallinity results in better optical transmittance, electrical conductivity and carrier mobility. Our
method therefore provides a simple yet effective way in optimizing the performance of AZO films, which is important for a range of optoelectronic and energy conversion applications.

2. Experimental procedure

AZO thin films were prepared on glass substrates by radio-frequency (RF) reactive magnetron sputtering using the Integrated Plasma-Aided Nanofabrication Facility (IPANF) [20]. Briefly, the glass substrates were cleaned thoroughly in acetone and ethanol and then dried in hot air prior to deposition. This cleaning step helps to improve the adhesion between the deposited films and the substrate. The substrates were then loaded into the magnetron sputtering chamber and the distance between the target and the substrates was fixed at 53 mm. A square Al₂O₃ chip (99.99% in purity) with an area of 1200 mm² placed on top of a ceramic ZnO target (99.99% in purity) served as the dopant source. When the base pressure was below 2x10⁻⁵ Torr, the substrates were cleaned for 10 min by Ar plasma (60 sccm) at a RF power of 95 W. Subsequently, the RF reactive magnetron sputtering was carried out with Ar and H₂ at flow rates of 60 and 7.5 sccm respectively, and the AZO films were deposited at 400 °C with a fixed RF power density of 5.0 W/cm². Finally, the deposited AZO thin films were annealed inside a quartz tube of a thermal furnace under a nitrogen atmosphere at 100, 200, 300, 400 and 500 °C for 2 hours.

The structural analysis was carried out by X-ray diffractometry (XRD, Philips X’Pert MRD) with the incident X-ray wavelength at 1.54 Å (Cu Kα), operated in a locked-couple (θ–2θ) mode. The electrical resistivity, Hall mobility and carrier concentrations were measured by the van de Pauw method at room temperature using the Bio-Rad HL5500PC system [21]. The optical transmission and reflection spectra were obtained by the UV–Vis spectrophotometer (Cary 510 Bio, Varian) in the wavelength range of 300 – 1100 nm.
3. Results and discussion

Annealing is known as an effective process which can significantly improve the properties of thin films [22-24]. As the temperature is increased, either by the application of substrate heating or post-growth heat treatment, thermal energy is provided for surface and bulk diffusions. Such diffusions release the internal strain of the microstructure caused by lattice mismatch or defects formed during growth, leading to the reorganisation of the microstructure and the improvement of crystallinity of the film. Consequently, one can expect several physical properties such as dielectric constant, effective carrier mass, carrier concentration and mobility to be altered [23, 24]. Our results in the following sections illustrate these effects.

3.1. Structural properties

The XRD spectra of AZO thin films annealed at different temperatures are shown in Fig. 1. Peaks at (002) and (101) could be identified in all the annealed films. Notably, the intensity of (002) peak increases as the annealing temperature increases up to 400 °C. These changes in peak intensity are related to the anisotropic nature of the AZO thin film structure, and indicate that the crystal structure reorganized preferentially in the (002) c-axis orientation during annealing [25]. The anisotropic nature has been reported previously [26] and can be interpreted using the Drift’s model of grain growth [27]. According to this model, the nucleations of all orientations are formed during the initial stage of film deposition. However there is a competition between the different growths directions. The growth direction with the fastest growth rate is expected to dominate as the film becomes thicker. The post-synthesis
annealing process magnifies the anisotropic structure of the film since the additional thermal energy facilitates film restructuring along its growth direction.

Based on the XRD results, the average grain size $D$, the distance between the crystalline planes $d_{002}$ and the lattice constant $c$ of the (002) orientation can be calculated. The grain size $D$ could be estimated by Scherrer formula [28],

$$D = \frac{K \lambda}{\beta \cos \theta}$$

(1)

where $K$ is material-specific Scherrer constant (assumed to be 0.9 for ZnO [29]), $\theta$ (in degrees) represents the Bragg angle of the (002) peak, $\lambda$ is the Cu K$_\alpha$ wavelength and $\beta$ (in radians) is the full-width-half-maximum (FWHM) of the (002) diffraction peak.

The distance $d$ between the crystalline planes of (002) could be extrapolated using Bragg’s law.

$$\lambda = 2d \sin \theta$$

(2)

In addition, the lattice constants $c$ could be extrapolated by the following formula [30],

$$d_{hkl} = \frac{1}{\sqrt{\frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2}}}$$

(3)

where $a$ and $c$ are the lattice constants and $d_{hkl}$ represents the crystalline plane distance for indices $(hkl)$ calculated in Eq. (2). The lattice constant $c$ is equal to $2d_{002}$ for the (002) diffraction peak.

The calculated results are shown in Table 1, which summarizes the effects on the AZO film’s crystal structure induced by post-synthesis annealing. By increasing the annealing temperature to 400 °C, the average grain size of the AZO thin films increased and the distance between the (002) plane decreased. It is also found that all $d$ values are larger compared to the interplanar spacing of the standard ZnO powder $d_0$, which is 0.2584 nm [15]. This is a sign of the incorporation of Al dopant atoms into the ZnO crystal structure.
At annealing temperatures above 400 °C, degradation of the crystalline properties is observed. The decrease in the average grain size and the increase in $d_{002}$ observed in this case could be attributed to the grain coarsening phase due to recrystallization within the grain boundary, leading to microstructures roughening [30]. The best film quality was therefore obtained by annealing at 400 °C.

3.2. Optical properties

Figure 2 shows the optical transmittance of the AZO thin films prepared under varying annealing temperatures from 100 to 500 °C. The optical transmittance shows an increase with the annealing temperature and the average value in the visible spectrum exceeds 80% when the films were annealed at 200 °C and above, as compared to 65% of the as-deposited films. The highest transmittance of approximately 88.5% was obtained when the film was annealed at 500 °C. The transmittance cut-off observed at the wavelengths below 300 nm was attributed to the onset of fundamental absorption and is consistent with previous results [22].

The optical absorption at the absorption edge corresponds to the energy level of the band gap, while the absorption in the visible region is related to local energy levels caused by intrinsic defects of the material. For a direct band gap semiconductor, the optical absorption coefficient $\alpha$ is calculated by the following expression [15],

$$I = I_0 \exp (-\alpha d)$$

(4)

where $I_0$ and $I$ denote the intensities of the incident and the transmitted light respectively, and $d$ is the film thickness. The value of $\alpha$ allows us to determine the optical band gap $E_{opt}$ through the relationship [11],

$$(\alpha \nu)^2 = A(\nu - E_{opt})$$

(5)
where \( \nu \) denotes the wavelength, \( h \) is Planck’s constant and \( A \) is a constant. By plotting \( hv \) versus \( (ahv)^2 \), the optical band gap \( E_{opt} \) can be extrapolated from the straight-line portion of the Tauc plot [31]. Thus the transmission cut-off wavelength can be estimated.

\[
\lambda_{\text{cutoff}} = \frac{hc}{E_{opt}}
\]  

(6)

The values of \( E_{opt} \) and the absorption edge of the AZO films post-processed at different annealing temperatures are shown in Table 2. From this table, there was a noticeable red-shift in the absorption edge of the films when the annealing temperatures increased from 100 to 400 °C. This red-shift from the ZnO systems was attributed to the renormalisation of the band gap arising from the presence of a higher concentration of free charge carriers [32], as elaborated in the next section. On the other hand, a reverse trend was observed in the films annealed at 500 °C, which was an indication of the reduction of free carrier concentrations [33].

3.3. Electrical properties

Transparent conductive ZnO films are known to feature \( n \)-type conductivity [34]. The electrical conductivity in AZO films is enhanced as compared to ZnO films because of the replacement of \( \text{Zn}^{2+} \) by \( \text{Al}^{3+} \) in the lattice structure. The Al dopants can generate extra electrons as free charge carriers and contribute to the improvement of electric conductivity. By obtaining the carrier concentration and Hall mobility, the resistivity \( \rho \) of the film can be calculated,

\[
\rho = \frac{1}{en\mu}
\]  

(7)

where \( e \) is the electric charge, \( n \) is the carrier concentration and \( \mu \) denotes the carrier mobility.
The electrical properties of the different annealed films are shown in Fig. 3 and the exact values are presented in Table 3. For films annealed at temperatures below 400 °C, we observed some improvements in the electrical characteristics. For example, the carrier concentration and the Hall mobility increased from $5.16 \times 10^{20} \text{ cm}^{-2}$ and $6.47 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to $8.25 \times 10^{20} \text{ cm}^{-2}$ and $13.43 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ respectively. We attributed the increase of the carrier concentration to the larger number of oxygen vacancies and the incorporation of Al dopants. On the other hand, the higher mobility was due to the annealing process which released the internal strain of the crystal structure caused by crystalline defects and grain boundaries. The improvement in the crystallinity of the film allowed a larger mean-free-path for the free carriers and thus led to an enhanced mobility. Consequently, the electrical resistivity of the annealed AZO thin films decreased to $5.63 \times 10^{-4} \text{ } \Omega \cdot \text{cm}$, as calculated using Eq. 7. It is noted that this value is comparable to that of ITO thin films prepared by magnetron sputtering [31].

However, upon further annealing at 500 °C, a decrease in the carrier concentration and mobility was recorded, leading to a reduction in the electrical conductivity. The observed degradation of the electrical properties is related to the coarsening of the film’s microstructure, as evidenced in the XRD results in Fig. 1. This coarsening behavior deteriorated the film quality and might also increase the number of defects present in the grain boundary, which in turn reduced the carrier concentration and mobility [35].

4. Conclusion

Transparent conducting AZO films were deposited by RF reactive magnetron sputtering and were annealed at temperatures from 100 to 500 °C. The XRD analysis indicated that the films were polycrystalline with a preferred $c$-axis orientation. By annealing the films at temperatures up to 400 °C, an increase in the grain sizes and the anisotropic
crystal orientation were observed. Such increase indicated an improvement of the film structure with the removal of structural defects and grain boundaries. However when the films were annealed at temperatures above 400 °C, coarsening of the microstructure was observed.

In addition, it was shown that the optical transmittance of AZO thin films in the visible region increased with the annealing temperatures. The average transmittances were found to be above 80% in the visible region for films annealed at 200 °C and above temperatures. A red-shift of the sharp absorption edge occurred along with the increased annealing temperature, indicating an increase of free carrier concentrations. Moreover, the alternation of the crystal structure also corresponded to the improvements of the electrical conductivity. The post-synthesis thermal treatment method, which is generally applicable to AZO thin films prepared by various methods, thus enables us to optimise the structural, electrical and optical properties of AZO films which may eventually replace the ITO films in many TCO applications.

Acknowledgements

The authors would like to thank Dr. I. Levchenko for technical assistance and helpful discussion. This work was partially supported by the National Research Foundation (Singapore) and CSIRO’s OCE Science Leadership Scheme.
References

[17] G. Fang, D. Li, B.L. Yao, phys. stat. sol. (a) 193 (2002) 139-152.
Figure Captions

**Fig. 1.** XRD spectra of the AZO thin films treated at different annealing temperatures.

**Fig. 2.** Optical transmittance of the annealed AZO thin films.

**Fig. 3.** Electrical properties of AZO thin films versus the annealing temperatures.

Table Captions

**Table 1.** XRD peak characteristics and structural parameters of the AZO films.

**Table 2.** Band gap and sharp absorption edge of the AZO thin films post-processed at different annealing temperatures.

**Table 3.** Electrical properties of AZO thin films before and after the annealing treatment.
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Fig. 2. Optical transmittance of the annealed AZO thin films.
Fig. 3. Electrical properties of AZO thin films versus the annealing temperatures.
Table 1. XRD peak characteristics and structural parameters of the AZO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$ (°)</th>
<th>FWHM (a.u.)</th>
<th>$d_{002}$ (nm)</th>
<th>$c$ (nm)</th>
<th>$D$ (nm)</th>
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<tr>
<td>As-deposited</td>
<td>34.2176</td>
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<tr>
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<td>0.27970</td>
<td>0.260623</td>
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<tr>
<td>500°C</td>
<td>34.3218</td>
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Table 2. Band gap and sharp absorption edge of the AZO thin films post-processed at different annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>$E_{opt}$ (eV)</th>
<th>Sharp absorption edge (nm)</th>
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<tr>
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<td>500</td>
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Table 3. Electrical properties of AZO thin films before and after the annealing treatment.

<table>
<thead>
<tr>
<th>Annealing temperature /°C</th>
<th>Resistivity/ (1x10^3 Ω.cm)</th>
<th>Carrier concentration/ (1x10^20 cm^-3)</th>
<th>Hall mobility/ (cm².V⁻¹.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>1.87</td>
<td>5.16</td>
<td>6.47</td>
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<td>100</td>
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