Effect of sputtering conditions on growth and properties of ZnO:Al films

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Abstract: Al-doped zinc oxide (AZO) films were deposited on glass substrates by mid-frequency magnetron sputtering. The effects of substrate rotation speed and target–substrate distance on the electrical, optical properties and microstructure and crystal structures of the resulting films were investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), spectrophotometer and Hall-effect measurement system, respectively. XRD results show that all AZO films exhibit a strong preferred c-axis orientation. However, the crystallinity of films decreases with the increase of substrate rotation speed, accompanying with the unbalanced grains grows. For the films prepared at different target–substrate distances, the uniform microstructure and morphology are observed. The highest carrier concentration of 5.9×10²⁰ cm⁻³ and Hall mobility of 13.1 cm²/(V·s) are obtained at substrate rotation speed of 0 and target–substrate distance of 7 cm. The results indicate that the structure and performances of the AZO films are strongly affected by substrate rotation speed.

Key words: ZnO thin film; mid-frequency magnetron sputtering; substrate rotation speed; target–substrate distance; optoelectronic performance

1 Introduction

Aluminum doped zinc oxide (AZO) is one of the most promising candidates for transparent semiconductive materials because of its excellent electrical conductivity and high optical transparency in the visible and near infrared region [1]. AZO films are generally used as window electrodes and have been widely applied in solar cells, light-emitting diode, flat panel display and other optoelectronic devices [2,3]. It is considered that deposition conditions play a crucial role in the growth of AZO films and thus show significant effect on these optoelectronic devices. Numerous studies have focused on the deposition parameters such as power, pressure, substrate temperature and deposition distance. DAGAMSEH et al [4] concluded that the crystallite size can be improved by varying the substrate temperature rather than the RF power and chamber pressure. Other group adjusted the deposition pressure to diminish ion bombardment effects on the film surface [5]. SHI et al [6] prepared AZO films with low resistivity of 7.5×10⁻³ Ω·cm at different sputtering powers.

In those cases of the thin film deposition, the microstructure and morphology as well as stoichiometry are in fact decided by the energetic conditions during plasma processing. For example, the substrate arrangement facing different target regions would lead to the inhomogeneous microstructure and optoelectronic properties [7]. In addition, there has been some sputtering position studies referring to the plasma conditions, locating at different target regions or using the rotatable target [8,9]. As a result, the plasma density at various locations is quite different and therefore the uneven property distribution across the substrates is inevitable for magnetron sputtered AZO films.

It is a common practice that the substrate holder rotates around its normal to achieve a uniform film. However, the substrate rotation speed and the effects of the plasma conditions are seldom mentioned for AZO films. Based on previous studies, we unexpectedly found that the structure and properties of AZO films are evidently degenerated after rotating the substrates when using ceramic targets. In this work, we examined the effects of substrate rotation speed ($R_s$) and target–substrate distance ($D_{ts}$) as well as their connection with...
the structural, electronic and optical properties of mid-frequency (MF) sputtered AZO films. The effect of the microstructure on the film performances was particularly discussed. Therefore, we can get a deeper insight into the relationship between the microstructure and properties of AZO films.

2 Experimental

AZO thin films were deposited on glass substrates by a MF sputtering system. A schematic diagram of the MF deposition system (SHENGPU sputtering source consisting of two cathodes operating at 40 kHz) and plasma distribution are illustrated in Fig. 1. High energy plasma is focused in front of the target by magnetic field and causes a non-uniform erosion. As an unbalanced magnetron, the low energy plasma disperses away from the target. A commercially available, sintered ceramic 2% Al$_2$O$_3$–ZnO target (corresponding to 1.1% Al in target, mass fraction) with dimensions of 300 mm×75 mm and 99.99% purity was applied as source materials. The chamber vacuum was evacuated to a base pressure of $4\times10^{-3}$ Pa. To obtain films with valuable properties, the pressure, plasma power and substrate temperature were optimized according to previous research [6]. In this experiment, films grew in atmosphere of pure Ar with constant pressure of 0.1 Pa at room temperature. The sputtering power was set to be 1800 W. To analyze the influence of substrate rotation speed ($R_s$), the substrates were placed on rotating holder at $R_s$ of 0, 2, 10 and 15 r/min, respectively. For considering the influence of target–substrate distance ($D_{ts}$), the substrates were placed in front of target at a sputtering power of 800 W and $D_{ts}$ of 7 or 10 cm. Before deposition, the Ar plasma was employed to clean the substrates for 5 min with an ion source at a power of 300 W and a bias voltage of 800 V. To eliminate the possible influence of thickness, all AZO films with identical thicknesses of 300–400 nm were maintained by adjusting deposition duration.

The phase structure of the as-deposited films was characterized by X-ray diffraction (XRD) using a Philips X’pert MPD diffractometer. The film thickness was measured by a TEKTAK XT profiler. The surface morphology was assessed by field-emission scanning electron microscopy (SEM) and the compositions were performed by energy dispersive X-ray spectroscopy (EDS). The root mean square (RMS) roughness was investigated by atomic force microscopy (AFM, Multimode Nanoscope–V) in scanAsyst mode. Optical measurements were made by an SP–752PC spectrophotometer and photon wavelengths ranged from 300 to 800 nm. The resistivity, carrier concentration and mobility were obtained by the four-probe van der Pauw method using Hall-effect measurement system (HL5500).

3 Results and discussion

3.1 Influence of substrate rotation speed

The phase structures of the Al-doped ZnO thin films were identified by X-ray diffraction. Figure 2 shows the XRD patterns of AZO films obtained at substrate rotation speeds of 0, 2, 10 and 15 r/min, respectively. All films exhibit one diffraction peak corresponding to the (002) orientation of ZnO (JCPDS 79–0208) with a hexagonal wurtzite structure. The diffraction intensities greatly reduce when $R_s$ increases from 0 to 2 r/min and then have a little increase after further increasing $R_s$. The results imply that grain growth lies on the substrate rotation speed and the highest crystallinity can be obtained at $R_s$ of 0. The average crystallite size in the range of 20–30 nm estimated from the XRD spectra is collected in Table 1.

There are two reasons for the improvement of crystallinity as a function of $R_s$. Firstly, the distribution
of sputtered species is uneven in the chamber as diagrammatized in Fig. 1. It is well known that the free energy of nucleation tends to decrease at high deposition rate, which favors to form a good growth film. It is readily observed that the deposition rate (61 nm/min) at $R_s$ of 0 is much larger than that (10 nm/min) at higher substrate rotation speeds. It is considered that the obtained high deposition rate is due to the increased flux of adatoms [10]. Furthermore, high energy of the sputtered species can be obtained by reducing the substrate rotation speed. It is clear that the substrate residence time in front of the target is reduced after increasing substrate rotation speed. Thus, there are more collision odds between the sputtered species and gas molecules before arriving at the substrate with high $R_s$, leading to the reduced energy of sputtered species. As a result, denser and (002) textured AZO films were formed at $R_s$ of 0 due to lower energy for nucleation and higher energy for film growth. The variation in the optoelectronic properties should be observed due to different crystal growth modes [11].

SEM images of the AZO films are shown in Fig. 3. The surface morphology reveals a noticeable transformation with increasing $R_s$. Polyhedral grains and smooth surface were clearly observed at $R_s$ of 0. However, the grains unbalanced grew with increasing the substrate rotation speed and the grain size was not as uniform as that at $R_s$ of 0. Once $R_s$ is up to 10 r/min, some comparatively large grains extrude out of the film surface. These scattered large grains are in size of 200 nm, which is 10 times bigger than that of the small one. This uneven distribution of the grain sizes should be caused by the crystal growth competition. When the substrate moved away from the target, the atoms had

<table>
<thead>
<tr>
<th>Substrate rotation speed/(r·min$^{-1}$)</th>
<th>Deposition rate/(nm·min$^{-1}$)</th>
<th>FWHM/(°)</th>
<th>Crystallite size/nm</th>
<th>Thickness/nm</th>
<th>Al content/%</th>
<th>Surface roughness/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61</td>
<td>0.317</td>
<td>29.3</td>
<td>324</td>
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<td>4.6</td>
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<tr>
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<td>14</td>
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<td>405</td>
<td>1.4</td>
<td>7.6</td>
</tr>
<tr>
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<td>9</td>
<td>0.442</td>
<td>19.3</td>
<td>270</td>
<td>2.4</td>
<td>12.9</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>0.425</td>
<td>21.4</td>
<td>297</td>
<td>2.0</td>
<td>21.9</td>
</tr>
</tbody>
</table>

**Table 1** Crystal structure parameters of AZO films deposited at different substrate rotation speeds

Fig. 3 SEM images of AZO films deposited at different substrate rotation speeds: (a) 0; (b) 2 r/min; (c) 10 r/min; (d) 15 r/min
more time for surface diffusion and thus favored the formation of the large grains. As a result, coarser structures of the films were obtained [12]. Based on morphology analysis, it is expected that surface roughness should change with substrate rotation speed.

Figure 4 shows AFM morphologies of the AZO films as a function of $R_s$. Corresponding to SEM results, the films at $R_s$ of 0 exhibit a smooth surface with uniform grain distribution. After increasing $R_s$ from 10 to 15 r/min, some excessively larger grains are observed. Those grains scatter with ambiguous boundaries. The measured root-mean-square (RMS) surface roughness values are 4.6, 7.6, 12.9 and 21.9 nm for the films deposited at $R_s$ of 0, 2, 10 and 15 r/min, respectively. It is known that high surface roughness may deteriorate the optoelectronic properties of the films. The variation in RMS roughness indicates the improved structure and optoelectronic performances can be obtained by adjusting $R_s$.

Al contents in AZO films are measured by EDS and the results are shown in Table 1. All films display a gradual increase of Al content compared with 1.1% Al (mass fraction) in the target. At $R_s$ of 10 r/min, the highest Al content of 2.4% is obtained and has no evident change after further increasing $R_s$. The increase of Al content could be attributed to lower sputtering threshold energy of Zn atoms. Al atoms with high energy possess high mobility during the sputtering process, leading to the overstoichiometry of Al in the films. Consequently, stoichiometric deviations of the films are considered to be the interactions of the sputtered species with the plasma environment [13]. It is known that the overstoichiometry of Al content has a negative effect on the microstructure and properties of the films. For instance, the high doping concentration may cause deterioration in the crystallinity. Inactive Al atoms segregate into grain boundaries, which can inhibit the crystallization and preferred orientation of ZnO [14]. Furthermore, Al$_2$O$_3$ is probably formed due to the excessive Al, leading to the increase of the resistivity [15].

Figure 5 illustrates the optoelectronic performance of the AZO films as a function of $R_s$. The results indicate that the films show slight variation in transmittances at different $R_s$, but all achieve above 80% transmittance in the visible light region. The absorption edge at 350 nm is recorded and the blue shift of the absorption edge is mainly attributed to the lifting of the Fermi level into the conduction band with the increase of carrier concentration [16]. The absorption edge shifts to the shortest wavelength at $R_s$ of 0 and the transparency near the absorption edge slightly decreases after further increasing $R_s$. Figure 5(b) gives values of the average transmittance, energy gap and resistivity as a function of

![Fig. 4 AFM images of AZO films at different substrate rotation speeds: (a) 0; (b) 2 r/min; (c) 10 r/min; (d) 15 r/min](image-url)
As a direct band gap n-type semiconductor, the optical energy gap ($E_g$) can be determined from the $(\alpha h\nu)^2$ versus $h\nu$ plot by extrapolating the linear portion of the curve to $\alpha h\nu = 0$ [17]. The optical energy gaps are evaluated to be 3.79, 3.5, 3.3 and 3.3 eV at $R_s$ of 0, 2, 10 and 15 r/min, respectively. Several studies proved that the band gap directly respected to carrier concentration [18−20]. The results indicate that a better electrical property can be obtained at $R_s$ of 0.

It can be seen in Table 2 that the electrical performances of AZO films are evidently influenced by substrate rotation speed. As $R_s$ increases from 0 to 15 r/min, the resistivity varies from 8.1×10$^{-4}$ to 5.0×10$^{-1}$ Ω·cm, increasing by three orders of magnitude. As is well known, the resistivity is proportional to the reciprocal of the product of carrier concentration and mobility. Therefore, the resistivity deterioration with increasing $R_s$ is attributed to the change of carrier concentration or mobility. At substrate rotation speed of 0, a carrier concentration of 5.9×10$^{20}$ cm$^{-3}$ and a Hall mobility of 13.100 cm$^2$/(V·s) are obtained. For the films deposited at $R_s$ of 15 r/min, the mobility is reduced to 0.835 cm$^2$/(V·s) with a carrier concentration of 1.4×10$^{19}$ cm$^{-3}$, implying that substrate rotation speed has a significant influence on the electrical properties.

Based on the above analysis, we consider that the film growth can be adjusted by substrate rotation speed and therefore determines its characteristics and properties. The intensities as well as the FWHM values of (002) peaks reveal that the crystallinity of the films is hindered by increasing $R_s$. Higher crystal orientation predicates better electrical properties, attributing to the reduction of the scattered carriers at the grain boundaries and crystal defects. XRD results reveal that there is a sharp degradation of the (002) peak value with increasing $R_s$ from 0 to 2 r/min, accompanied with a huge increase of resistivity from 8.1×10$^{-4}$ to 2.4×10$^{-2}$ Ω·cm. Furthermore, the grains are uniform with dense and smooth surface when the films are deposited at $R_s$ of 0. This smooth microstructure contains fewer pores and projections, which act as traps for the free carriers and barriers for transporting the carriers in the films [21]. In addition, it is suggested that large surface roughness increases the number of oxygen traps and favors the adsorption of oxygen, leading to the increase of resistivity [17]. As a result, good crystal quality and electric properties can be obtained for the films deposited at $R_s$ of 0.

### 3.2 Influence of target–substrate distance

Except for substrate rotation speed, the distance between the substrate and target is considered to be an important parameter for the preparation of AZO films deposited by magnetron sputtering technology [22]. Figure 6 displays XRD patterns of the AZO films deposited at $D_{ts}$ of 7 and 10 cm, respectively. Only the peaks indexed to (002) and (004) reflection of the hexagonal wurtzite structure ZnO can be observed and the intensities are relatively the same. The crystal parameters obtained from XRD spectra are shown in Table 3, from which the gain sizes at $D_{ts}$ of 7 and 10 cm are 26 and 28 nm, respectively.

SEM images of the AZO films at different target–substrate distances are given in Fig. 7. The films delivered a uniform and smooth surface with even grain size. The Al contents in the films are kept at 1.3% and 1.1% at $D_{ts}$ of 7 and 10 cm, respectively, very close to that of the target. The plasma density and atom energy

<table>
<thead>
<tr>
<th>Rotating speed ($r\text{min}^{-1}$)</th>
<th>Resistivity/Ω·cm</th>
<th>Carrier concentration/cm$^{-3}$</th>
<th>Hall mobility/(cm$^2$·V$^{-1}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.1×10$^{-4}$</td>
<td>5.9×10$^{20}$</td>
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</tr>
<tr>
<td>2</td>
<td>2.4×10$^{-2}$</td>
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<td>10</td>
<td>6.7×10$^{-2}$</td>
<td>3.7×10$^{19}$</td>
<td>2.490</td>
</tr>
<tr>
<td>15</td>
<td>5.0×10$^{-1}$</td>
<td>1.4×10$^{19}$</td>
<td>0.835</td>
</tr>
</tbody>
</table>
decrease with increasing sputtering distance. During the sputtering process, there are positive or neutral particles which can lead to bombardments of deposited thin films and may cause re-sputtering, resulting in a decrease of the film thickness. Furthermore, it is suggested that the atoms with high energy would lead to the re-sputtering of Zn atoms from the substrate surface of 7 cm, thus providing a little higher Al content. These measurements show that the target–substrate distance does not clearly affect the crystal structure and composition of the films, indicating the slight variation in optoelectronic properties.

Optical results show the overlapping transmission spectra in the visible range of 450–900 nm, reaching an average transmittance of 85% in Fig. 8(a). The band gap of the films decreases from 3.65 to 3.46 eV at $D_s$ of 7 cm.

### Table 3 Crystal structure parameters of AZO films deposited at different deposition distances

<table>
<thead>
<tr>
<th>Deposition distance/cm</th>
<th>Thickness/nm</th>
<th>FWHM/(°)</th>
<th>Crystallite size/nm</th>
<th>Al content/%</th>
<th>Transmittance/%</th>
<th>Resistivity/($\Omega \cdot cm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>150</td>
<td>0.319</td>
<td>28.8</td>
<td>1.3</td>
<td>85</td>
<td>$8.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>270</td>
<td>0.342</td>
<td>26.2</td>
<td>1.1</td>
<td>84</td>
<td>$3.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 6 XRD patterns of AZO films deposited at different deposition distances

![XRD patterns of AZO films deposited at different deposition distances](image)

![SEM images of AZO films deposited at deposition distances of 7 cm (a) and 10 cm (b)](image)

Fig. 7 SEM images of AZO films deposited at deposition distances of 7 cm (a) and 10 cm (b)

Fig. 8 Transmittance (a) and optical band gap (b) curves of AZO films deposited at different deposition distances

![Transmittance (a) and optical band gap (b) curves of AZO films deposited at different deposition distances](image)
and 10 cm, as shown in Fig. 8(b). Compared with substrate rotation speed, target–substrate distance presents only a slight influence on the electrical properties. The resistivity values of $8.5 \times 10^{-2}$ and $3.6 \times 10^{-3} \ \Omega \cdot cm$ are achieved when the deposition distances are 7 and 10 cm, respectively. Generally, the variation of optoelectronic properties is own to different microstructures of the films. In the present experiment, the substrates were arranged at the same location but different sputtering distances. As described in Figs. 6 and 7, the crystallinity and surface morphology of the films are similar to each other except for the Al content. We therefore consider that the small increase of resistivity may be caused by the variation of Al content. The small Al content means a lower carrier concentration, therefore leading to a higher resistivity.

It can be seen that substrate rotation speed and target–substrate distance play different roles in the electrical, optical and structural properties of MF sputtered AZO films. Further researches on the sputtering distance determine the important influence of substrate rotation speed on the microstructure and electric properties of the films. The above mentioned results indicate that the crystallinity of AZO films can be improved by adjusting sputtering parameters including substrate rotation speed and target–substrate distance, therefore promoting the optoelectronic properties of the AZO films.

4 Conclusions

1) Al-doped ZnO films were deposited by MF sputtering at different $R_s$ and $D_{ss}$ values. The deteriorated crystallinity and surface morphology are clearly observed at high $R_s$ and the resistivity showed the same trend.

2) The identical microstructure and Al content are observed at different $D_{ss}$ values, indicating that the characteristics of the AZO films are affected more greatly by $R_s$ rather than $D_{ss}$.

3) The resistivity and transmittance measurements clearly confirm that the best optoelectronic performance can be achieved at $R_s$ of 0 and $D_{ss}$ of 7 cm.

References


溅射条件对 ZnO:Al 薄膜生长和性能的影响

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摘 要：采用中频磁控溅射法在玻璃基体上制备 Al 掺杂 ZnO 薄膜（AZO），分别利用扫描电子显微镜（SEM）、原子力显微镜（AFM）、X 射线衍射仪（XRD）、分光光度计及霍尔测试系统研究不同沉积条件如样品台转速和靶—基距离对薄膜光学、电学、微观形貌及晶体结构的影响。XRD 结果表明，所有 AZO 薄膜都呈 c 轴择优取向，薄膜的结晶度随着样品台转速的增大而降低，且晶粒呈非平衡状态生长。而在不同的靶—基距离时，薄膜具有相似的微观结构和表面形貌。当样品台转速为 0、靶—基距离为 7 cm 时，AZO 薄膜的光电性能最好，载流子浓度和霍尔迁移率分别为 5.9×10²⁰ cm⁻³ 和 13.1 cm²/(V·s)。研究结果表明，样品台转速是影响 AZO 膜的结构和性能的主要因素。

关键词：ZnO 薄膜；中频磁控溅射；样品台转速；靶—基距离；光电性能

(Edited by Wei-ping CHEN)