Structural evolution, electrical and optical properties of AZO films deposited by sputtering ultra-high density target

JIWEN XU^{1,2}, ZUPEI YANG^{1,*}, HUA WANG² and XIAOWEN ZHANG²

¹School of Material Science and Engineering, Shaanxi Normal University, Xi'an 710062, China

²School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

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Abstract. Aluminum-doped zinc oxide (AZO) target was fabricated using AZO nanopowders synthesized by co-precipitation method and then the AZO films with different thicknesses were deposited on glass by d.c. magnetron sputtering at room temperature. AZO target is nodules free and shows homogeneous microstructure, ultra-high density and low resistivity. ZnAl_2O_4 phase appears in AZO target and disappears in AZO films. All AZO films show *c*-axis preferred orientation and hexagonal structure. With increasing film thickness from 153 to 1404 nm, the crystallinity was improved and the angle of (002) peak was close to 34.45° . The increase in grain size and surface roughness is due to the increase in film thickness. The decrease of resistivity is ascribed to the increases of carrier concentration and Hall mobility. The lowest resistivity is $9.6 \times 10^{-4} \Omega\text{-cm}$. The average transmittance of AZO films exceeds 80%, and a sharp fundamental absorption edge with red-shifting is observed in the visible range. The bandgap decreases from 3.26 to 3.02 eV.

Keywords. AZO film; ultra-high density; ceramic target; nanopowders; evolution.

1. Introduction

Transparent conducting oxide (TCO) films such as Sn-doped In_2O_3 (ITO), Al- or Ga-doped ZnO (AZO or GZO) and F-doped SnO_2 (FTO) have high conductivity and transmittance and have been heavily studied for their applications in light-emitting diodes, organic light-emitting diodes, liquid crystal displays, touch panels and thin film solar cells (Katayama 1999; Klutha *et al* 1999; Kima *et al* 2001; Taka *et al* 2002; Lei *et al* 2010; Park *et al* 2011). For TCO films fabrication, magnetron sputtering is a mature technology, because of low growth temperature, high growth rate, high quality and easy for large area coating (Swann 1998). Therefore, the alloy or ceramic targets become the key material required. Alloy target used for AZO films is more sensitive to minor changes of sputtering parameters (e.g. oxygen partial pressure or flow rate) (Kawada 1990). Ceramic target instead of alloy target can resolve the above unstable problem. However, the arcing and nodules formation on the target surface near or sometimes in the erosion race-tracks (Ishibashi *et al* 1990; Omata *et al* 2006) weakens the advantages of ceramic target. The formation of nodules results in reducing growth rate and particulate contamination which degenerates film quality. The coating system has to be shut down frequently for cleaning

nodules. Formation of nodules on target surface is therefore highly undesirable. The most important way to reduce nodules is to increase the target density and decrease the composition inhomogeneous distribution (Nadaud *et al* 1994; Nakashima and Kumahara 2002).

AZO films were deposited mainly using AZO ceramic target in recent studies. To optimize performance of AZO films, such as resistivity, transmittance and texture surface, many researchers (Dewald *et al* 2009; Li *et al* 2009; Hsu *et al* 2010) focussed on the influences of sputtering parameters, such as doping elements and concentration, growth temperature, power, pressure, atmosphere, power supply, annealing and buffer layer. However, how to prepare high-quality target and the correlation between target and film are rarely focussed, which have prevented the optimization of AZO film.

In the present paper, AZO films have been mainly used in CIGS and Si thin film solar cells as transparent and conductive front contact layer because of their cheap and abundant raw materials as well as excellent electrical and optical properties (Kaelin *et al* 2004; Tark *et al* 2011). If the thickness of AZO film can be thinned and the conductivity is not be reduced, which not only benefits materials saving, but also decreases light absorption.

In this work, ultra-high density AZO target was fabricated using high sintering activity powders. The effects of thickness on the structural evolution, electrical and optical properties of AZO films prepared by ultra-high density target were investigated.

*Author for correspondence (yangzp@snnu.edu.cn)

2. Experimental

AZO powders were prepared by co-precipitation method using the aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with 5 at% doping (Al/Zn atomic ratio). After preparing 0.2 mol/L (Zn^{2+} ion concentration) aqueous solution, 3 mol/L ammonia was then slowly dropped to the aqueous solution under vigorous stirring until pH value reached 8. The precipitate was washed using distilled water to remove NO_3^- ions and then dispersed with ethanol. AZO powders were obtained by calcining the precipitates at 600 °C for 2 h. The green body was pressed and compacted by cold isostatic pressing (250 MPa). AZO target was sintered at 1400 °C for 4 h in air. For observing grain boundary and size, the target was thermally etched at 1200 °C for 1 h in air.

AZO films were deposited on glass substrate by d.c. magnetron sputtering at room temperature after 5 min pre-sputtering. The chamber base pressure was 8×10^{-5} Pa, the discharge gas was argon without introducing oxygen. The power was 100 W and working pressure was 1.5 Pa. AZO films with thicknesses of 153, 414, 689 and 1404 nm were prepared by controlling sputtering time.

The grain size, surface and cross-section morphology were analysed by scanning electron microscope (SEM, JSM-5610LV, JEOL). The three-dimensional structure and roughness were observed by atomic force microscope (AFM, SPI3800N, Seiko). The composition was identified by energy-dispersive X-ray spectroscopy (EDS, Thermo NORAN vantage IV). The phase structure was characterized by X-ray diffraction (XRD, D8-ADVANCE, Bruker). The particle size distribution was measured by laser particle size analyser (Nanotrac TM150, Microtrac). The thickness was measured by profilometer (XP-Plus 100, Ambios). The resistivity, carrier concentration and mobility were measured by hall effect measurement system (HMS-3000, Ecopia) at room temperature. The visible transmittance was measured by spectrophotometer (VIS 723G, China).

3. Results and discussion

3.1 Structure characteristics of AZO target

Figure 1 shows particle morphology and size distribution of the as-synthesized AZO powders. The inset SEM image shows that the grain shape is quasi-spherical and particle size is about 85 nm. However, the particle size distribution shows that the median diameter (D_{50}) is 67 nm and the most particle size is smaller than 100 nm. The particle size by SEM is larger than that by laser particle size analyser. This difference is ascribed to the weaker agglomerates among particles in the observed SEM powder. AZO nanopowders have high sintering

activity, which can promote the densification of sintering body during sintering process. Figure 2 displays XRD patterns of the AZO powders and target and the inset shows surface image of the eroded target. XRD patterns indicate that the AZO powders and targets are polycrystalline and hexagonal structures. However, the diffraction peaks (marked with $\rightarrow$) originating from the ZnAl_2O_4 phase are also observed in figure 2. The phase content in AZO target is composed of 97% ZnO (hexagonal) and 3% ZnAl_2O_4 (cubic). ZnAl_2O_4 phase is insulator, which decreases conductivity of the AZO target. Since the solubility of the aluminum atoms in ZnO matrix is very small, the aluminum atoms easily react with ZnO to form the ZnAl_2O_4 phase during sintering process (Shirouzu *et al* 2007; Hélène *et al* 2009;

Figure 1. Particle morphology and size distribution of AZO powders.

Figure 2. XRD patterns of AZO powders and target, and eroded target surface (inset).

Zhang *et al* 2012). ZnAl_2O_4 phase is also observed in other fabrication processes such as hot pressing, hot isostatic pressing and slip casting (Long *et al* 2004; Sun *et al* 2009; Wang *et al* 2011). The inset shows that the target surface is nodule and particle free, which is due to the ultra-high density and low resistivity. The density is 99.3% TD (theoretical density) and the resistivity is $2 \text{ m}\Omega\cdot\text{cm}$. The density and resistivity in this work are slightly better than the commercial target with a density of >95–99% TD and resistivity of $<7 \text{ m}\Omega\cdot\text{cm}$ (Sittinger *et al* 2009).

AZO target sintered at 1400°C exhibits dense structure with a few small pores as shown in figure 3. Spherical closed pores are entrapped primarily at the triple-grain points and the size of these pores is about $1 \mu\text{m}$. However, the pores are invisible in grains. The ZnO grains are tightly packed and grain cleavage is invisible in the fracture surface as shown in figure 3(b). Figure 3 also clearly shows that the ZnAl_2O_4 phase (off-white regions) coexists with ZnO phase (dark regions) in the sintered body and the ZnAl_2O_4 phase homogeneously distribute in the ZnO matrix. The size of ZnO and ZnAl_2O_4 grains is

about 5 and $1 \mu\text{m}$, respectively. The small grain size can improve sputtering rate and uniformity. ZnO and ZnAl_2O_4 phase in figure 3(b) are further confirmed by EDS as shown in figure 4. It can be seen that the intensity of the Al energy peaks at spot 1 is stronger than that at spot 2. The aluminum and zinc atom contents at spot 1 are 24.5 at% Al and 16 at% Zn and the contents at spot 2 are 2.2 at% Al and 46.1 at% Zn. The atomic ratio of Al/Zn at spot 1 is close to the ratio of 2 in ZnAl_2O_4 phase and the ratio of 4.8% at spot 2 is close to 5 at% doping level in the solution. These results indicate that the compositions at spots 1 and 2 are ZnAl_2O_4 and ZnO phases, respectively.

3.2 Structure characteristics of AZO films

Figure 5 displays XRD patterns of AZO films as a function of film thickness. Compared with the XRD patterns of AZO target, only (002) peaks exist in the XRD patterns for AZO films and no peaks of the ZnAl_2O_4 phase are observed. Therefore, AZO films show preferred orientation of *c*-axis perpendicular to the substrate surface. The *c*-axis preferred orientation can be elucidated by the ‘grain boundary movement’ model proposed by Lodder *et al* (1983). According to this model, at the very first stage of film growth, certain grains with a particular orientation start to grow. By thermodynamical coalescence of crystallites during film growth, oriented growth is achieved. The angle of (002) peak is smaller than the standard diffraction angle of 34.45° . This may be due to the ionization of ZnO or Al doping as reported by Kuroyanagi (1989) and Chun *et al* (2010). With increasing film thickness, the intensity of (002) peak increases and the angle gradually shifts to a high angle and is more close to the standard diffraction angle as shown in figure 5(b). The angle of (002) peak which is lower than the standard diffraction angle in this work is due to the residual tensile stress in AZO films rather than the ionization of ZnO or Al doping. Shifting towards high angle indicates that the (002) interplanar spacing (d_{002}) becomes small and approaches to the d_{002} of single crystal zinc oxide. Since the AZO films are deposited on amorphous glass substrate, large strain exists in AZO film because of lattice mismatch, which leads to the increase of d_{002} . The crystallinity of the thicker AZO film can be improved by deposition onto the former low crystalline layer. Hence, the stress in grain is reduced and d_{002} decreases with increasing film thickness.

The surface morphology of AZO films as a function of film thickness and the cross-section morphology of the 1404 nm AZO film are shown in figure 6. It can be seen that the air side of AZO film is smooth on the entire surface. The cross-section morphology exhibits columnar structure perpendicular to the substrate. These columnar grains also indicate that the crystalline film is obtained on the amorphous glass substrate. Some small

Figure 3. Fracture images of (a) as-prepared target and (b) thermally etched target at 1200°C for 1 h in air.

Figure 4. EDS spectra at (a) spot 1 and (b) spot 2 in figure 3(b).

Figure 5. XRD patterns of AZO films at angle of (a) 20–80° and (b) 33–36°.

Figure 6. Cross-section morphology of the 1404 nm AZO film and surface morphology of AZO films with different thickness of (a) 153, (b) 414, (c) 689 and (d) 1404 nm.

Figure 7. AFM images of AZO films with different thicknesses of (a) 153, (b) 414, (c) 689 and (d) 1404 nm.

Figure 8. EDS spectrum of the 1404 nm AZO film.

grains are observed for the 153 nm AZO film. However, larger grains are observed for the 414, 689 and 1404 nm AZO films. The grain size of the 153 nm AZO film is about 97 nm. With increasing film thickness, the grain size increases to 127, 194 and 290 nm, respectively. This suggests that the diffusion and transfer ability of surface atoms are improved with increasing film thickness, which leads to accelerated crystallization of AZO films and hence, the enhancement of grain size. The three-dimensional surface structure and roughness is also investigated by AFM as shown in figure 7. It can be seen that the size of grain clusters increases with increasing film thickness. All AZO films show homogenous grains distribution with individual columnar grains extending upwards. In addition, the roughness increases from 0.34 to 10.54 nm, when the film thickness increases from 153 to 1404 nm. The increase of roughness with increasing film thickness mainly results from the corresponding change in grain size.

The elemental content of the 1404 nm AZO film is investigated by EDS as shown in figure 8. EDS results show that the Zn, Al and O elements are present in AZO film. Si and Ca elements are not expected to be in the film and this may have resulted from the glass substrate. The data obtained by EDS illustrate that the 1.9 at% Al and 45.7 at% Zn in AZO film is close to the ratio of 4.8 at% in the AZO target.

3.3 Electrical characteristics of AZO films

Figure 9 shows resistivity (ρ), carrier concentration (n_c) and Hall mobility (μ) as functions of film thickness. The resistivity is $5.1 \times 10^{-3} \Omega\cdot\text{cm}$ for the 153 nm AZO film and then it dramatically decreases to $9.7 \times 10^{-4} \Omega\cdot\text{cm}$ for the 1404 nm AZO film. Guilléna and Herrero (2010) and

Zhu *et al* (2012) reported similar relationship between thickness and resistivity with increasing thickness from 100 to 1100 nm. The resistivity of $9.7 \times 10^{-4} \Omega\cdot\text{cm}$ is inferior to $3.13 \times 10^{-4} \Omega\cdot\text{cm}$ for AZO films deposited in 5% H_2 ambient reported by Zhu *et al* (2012). However, the lowest resistivity in our work is better than $1.6\text{--}2.0 \times 10^{-3} \Omega\cdot\text{cm}$ for AZO films deposited at almost same sputtering parameters as reported by Guilléna and Herrero (2010). The carrier concentration is $2.3 \times 10^{20} \text{cm}^{-3}$ for the 153 nm AZO film, then, increases to $7.7 \times 10^{20} \text{cm}^{-3}$ for the 1404 nm AZO film. It is noticeable that, for thinner AZO film, poor crystalline and large stress may exist in the AZO layer, which leads to lots of defects. Many free electrons then are caught by large numbers of traps formed by these defects. The Hall mobility increases from 5.3 to $8.4 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with increasing film thickness, which is mainly due to the enhancement of the crystalline and grain size. This suggests that in polycrystalline AZO film, the mobility is mainly affected by the scattering associated with imperfections such as grain boundaries or dislocations. Therefore, the decreasing resistivity with increasing film thickness is attributed to the increase of carrier concentration and Hall mobility.

3.4 Optical characteristics of AZO films

Figure 10 shows transmittance (including substrate) of AZO films in visible range as a function of film thickness and the inset shows the bandgap. All AZO films are uniform and transparent under naked-eye observation. The average transmittance of AZO films exceeds 80% in the range of 400–900 nm. With increasing film thickness, the transmittance slightly decreases because of thickness effect. Strong oscillations in transmittance curves are

observed clearly in the range of 400–900 nm, which is due to the constructive or destructive light interference at different wavelengths by multiple internal reflections between AZO/air and AZO/glass interfaces. The interference is more obvious for thicker AZO films. When thickness exceeds a certain value ($\gtrsim 180$ nm), the interference ripples will occur in transmittance spectrum due to etalon interference effects produced between air/film and film/substrate interfaces (Manifacier *et al* 1976). The bandgap for direct interband transition is given by Ziegler *et al* (1981) as follows:

$$\alpha h\nu = C(h\nu - E_g)^{1/2},$$

where C is a constant, α the optical absorption coefficient. The photon energy at the point where $(\alpha h\nu)^2$ is zero is E_g and can be determined by extrapolation of the $(\alpha h\nu)^2$ vs $(h\nu)$ curve. With increasing film thickness, the bandgap in inset shows red-shifting because of thickness

effect. The bandgap decreases from 3.26 to 3.02 eV with increase of film thickness from 153 to 1404 nm, respectively.

4. Conclusions

AZO powders were synthesized by co-precipitation method and then AZO target was prepared using as-synthesized powders. The powders are quasi-spherical with average diameter of 67 nm. The target shows ultra-high density of 99.3% TD and low resistivity of 2 m Ω ·cm. The phase structure of the AZO target is composed of 97% ZnO (hexagonal) and 3% ZnAl₂O₄ (cubic). ZnAl₂O₄ phase mainly distributes in ZnO grain boundaries. The eroded target surface is nodule and particle free. AZO films with different thicknesses deposited using ultra-high density target show hexagonal structure and c -axis preferred orientation. The thickness increases from 153 to 1404 nm, the grain size increases from 97 to 290 nm, and the roughness increases from 0.34 to 10.54 nm. The resistivity of AZO films decreases from 5.1×10^{-3} to 9.7×10^{-4} Ω ·cm. The transmittance of AZO films exceeds 80% in visible range and the bandgap in the range of 3.02–3.26 eV and shows small red-shifting.

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Figure 9. Resistivity, carrier concentration and Hall mobility of AZO films with different thicknesses.

Figure 10. Transmittance of AZO films with different thicknesses in visible range and band gap (inset).

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