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Effects of Substrate Temperature and Sputtering Power on the Optical and Electrical Properties of Al-doped Zinc Oxide Thin Films by Reactive RF Magnetron Sputtering

Peijie Lin, Yunfeng Lai*, Xiaoqin Ding, Shuying Cheng

School of Physics & Information Engineering, Fuzhou University, Fuzhou 350116, PR China.
Yunfeng.lai@fzu.edu.cn

Al doped zinc oxide (AZO) thin films were deposited on glass substrates with radio frequency (RF) magnetron sputtering. The influence of substrate temperature (*Ts*) and RF power (*Pw*) on the structural, optical and electrical properties of the AZO films were investigated. The X-ray diffraction patterns show that AZO films deposited over 100°C have hexagonal-wurtzite phase structures with highly c-axis preferred orientations, and the average crystal size increases upon the promotion of the *Ts*. When the *Ts* increases from room temperature (RT) to 250℃, the transmittance and the optical band gap of the AZO films increase slightly, whereas the resistivity decreases. The sputtering power also has a strong effect on the resistivity. As the sputtering power increases from 70 to 140W, the resistivity firstly decreases to the minimum at the power of 110W, and then it increases. It is also found that annealing is an effective way to decrease the resistivity of the AZO thin films (*Ts*=250°C and *Pw*=110W) from ~2×10-1 to ~3×10-3 Ω·cm.

1. Introduction

Zinc oxide (ZnO), a direct-band II-VI semiconductor, has fueled a great deal of attentions for its ferroelectric and ferromagnetic properties [Liu C, et al (2005) reported]. Due to its unique wide band gap and tunable electrical conductivity, ZnO could also be used as transparent electrodes for optic-electrical devices such as solar cells [Singh Sukhvinder, et al (2007) reported, Yin Zongyou, et al (2014) reported]. However, pure ZnO usually contains various intrinsic defects (O-vacancies and Zn-interstitial sites) [Fu En Gang, et al (2004) reported, Chen H X, et al (2010) reported] and thus poor electrical conductivity is exhibited, which is a huge obstruction for its electrode applications in electronic devices, especially for transparent electronics. Al doping into ZnO films (AZO) seems to be a feasible way to solve this problem. The doped Al atoms could substitute Zn atoms or occupy the interstitial sites, the defect environments could thus be changed with an improved electrical conductivity [Shin Seung Wook, et al (2010) reported, Fiddes A J, et al (2006) reported]. Additionally, AZO thin films have advantages of good thermal stability, high transmissivity and reserves abundance for the composed elements over the commonly used transparent conductive oxides (TCO) such as indium tin oxides (ITO). Furthermore, AZO thin films are suitable for various deposition techniques [Ekem N, et al (2009) reported, Li B S, et al (2002) reported]. Among them, radio frequency (RF) magnetron sputtering possesses good reproducibility in thin film parameters and is compatible to mass production. Therefore, we deposit Al doped ZnO films (AZO) by RF magnetron sputtering and also investigate the effect of sputtering power (Pw) as well as substrate temperature (Ts) on the properties of the films.

2. Experiment

AZO films were deposited on glass substrates in a magnetron sputtering system by a Zn-Al (Al=2 at.%) alloy target. In order to obtain a clean surface, the glass substrates were ultrasonically cleaned in acetone, and then rinsed in alcohol followed by rinsing in deionized water. The base pressure of the chamber was about 5×10-4 Pa. Before deposition, the target was pre-sputtered for at least 10 min to remove the contaminations. During the deposition, the total pressure (mixture of argon and oxygen) was kept at 0.5 Pa with 0.04 Pa as oxygen partial pressure. Other deposition parameters are shown in Table 1. After the deposition, some samples were annealed

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in nitrogen at 400℃ for 1 hour in order to study the effects of annealing on the electrical properties of the AZO films.

The crystal structures of the thin films were characterized by a X-ray diffractometer (XRD) (Panalytical, X-pert, Cu*Kα*, *λ*=1.5406Å), the film thickness was measured with a stylus surface profiler (KLA-Tencor D-100), the surface morphology was studied using an atom force microscope (CSPM5000s), the optical properties were measured by a spectrophotometer (Lambda35UV/VIS) and the electrical properties were acquired by a Hall-effect measurement system (Ecopia HMS-300).

Table 1: Deposition parameters of the AZO films

Sample name	*Pw* (W)	*Ts* (℃)
AZO-1	110	RT
AZO-2	110	100
AZO-3	110	150
AZO-4	110	200
AZO-5	110	250
AZO-6	70	200
AZO-7	90	200
AZO-8	125	200
AZO-9	140	200

3. Results and discussions

3.1 Microstructure

Fig.1 shows the XRD patterns of the films (AZO-1, AZO-2 , AZO-3, AZO-4 and AZO-5) deposited at different substrate temperatures. All the films are approximately in the same thickness (150±10 nm). The films exhibit an obvious XRD peak corresponding to the plane (002) of AZO with the structure of hexagonal (Joint Committee on Powder Diffraction Standards, JCPDS card 03-1060). The corresponding average crystal size (*D*) increases with a raising *Ts*, which results in a crystallinity improvement [Kang S J, et al(2007)]. Table 2 shows the detail parameters of the (002) diffraction peaks of the samples. It can be seen that, with the increasing of the *Ts*, FWHM of the (002) peak decreases and reaches a minimum of ~0.204° at a *Ts* of 250°C, which indicates that 250°C is suitable for depositing AZO films with a better crystal quality.

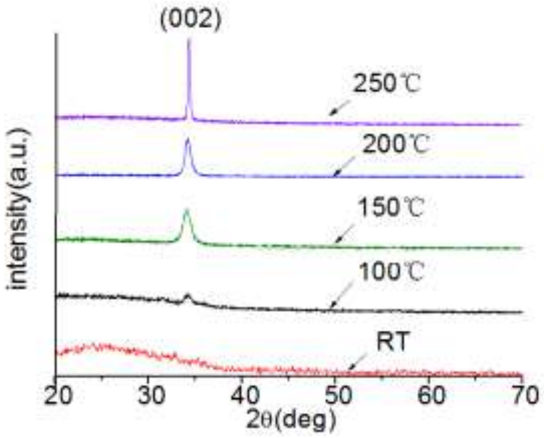

Figure 1: XRD patterns of the as-deposited AZO films with different substrate temperatures

Table 2: Parameters of (002) diffraction peaks of the AZO films

Sample name	*Ts* /°C	FWHM /deg	*D* /nm
AZO-2	100	0.823	9.85
ZO-3	150	0.734	11.03
AZO-4	200	0.326	24.92
AZO-5	250	0.204	40.31

3.2 Surface morphology

Fig. 2(a)-2(c) show the surface morphologies of the AZO films (AZO-1, AZO-3 and AZO-5) deposited at different substrate temperatures (*Pw*=110W). The sample surfaces seem to be covered with many small nano-sized grains. As the *Ts* increases from RT to 150℃, the root mean square roughness (*Rq*), probably attributed to the accelerative surface diffusion [Hong R J, et al (2003) reported], slightly decreases with a quite similar surface morphology obtained at room temperature. However, with a further increase of the *Ts* up to 250℃, bigger grains and greater *Rq* could be observed as shown in Fig. 2(c).

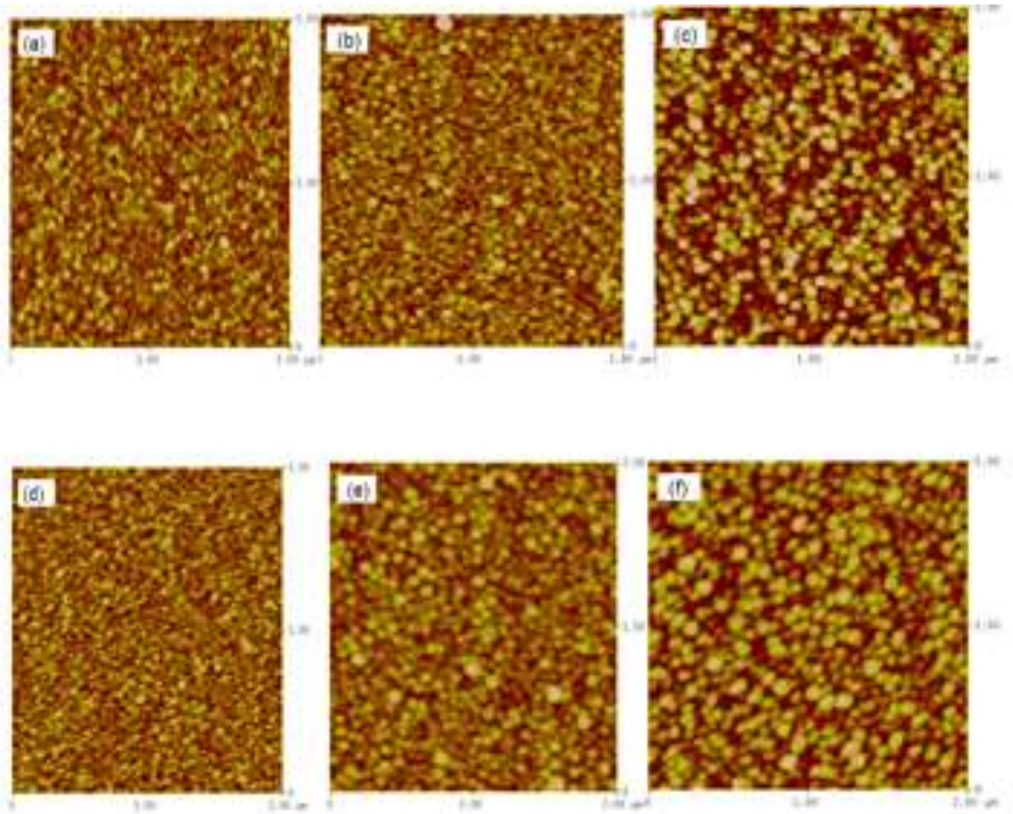

Figure 2: AFM images of the as-deposited AZO films with different deposition parameters: (a) Ts =RT, Rq =3.01nm; (b) Ts =150℃, Rq =2.97nm; (c) Ts =250℃, Rq =5.43nm; (d) Pw=70W, Rq = 2.83nm; (e) Pw =110W, Rq =4.93nm; (f) Pw=140W, Rq =6.95nm

Fig. 2(d)-2(f) show the AFM images of the AZO films (AZO-4, AZO-6 and AZO-9) deposited with different *Pw* (*Ts*=200℃). The surface morphology varies significantly and the *Rq* increases with an increasing *Pw*. Normally, the crystalline growth in a preferred orientation would be predominant at certain temperature regions. Additionally, the higher power provides energy to surface atoms and further contributes to the preferred oriented-growth [Sayago I, et al (2005) reported], which possibly produces a surface with a greater *Rq*.

3.3 Optical properties

Fig. 3(a) shows the transmittance and reflectance spectra of the AZO films (AZO-1, AZO-2, AZO-3, AZO-4 and AZO-5) deposited at different *Ts*. The transmittance increases with an increasing *Ts* from RT to 250℃. A sharp absorption edge in the transmittance spectra is observed in the wavelength range of 370–380 nm whose corresponding photon energy is equal to the band gap of bulk ZnO. Absorption coefficient (α) can be estimated from the optical spectra and be given by [Moszkowskrf S A, et al (1954) reported]:

$$\alpha = \frac{1}{d}\ln\left(\frac{\sqrt{(1-R)^4+4T^2R^2}-(1-R)^2}{2TR^2}\right) \tag{1}$$

where *d* is the thickness, *R* and *T* respectively indicate the reflectance and the transmittance. For a direct band gap material, the absorption coefficient as a function of the photon energy is expressed as the following equation

$$\alpha hv = A(hv - E_g)^{0.5} \tag{2}$$

where *A* is a constant, *hv* is the incident photon energy and *Eg* is the band gap energy.
The band gap energy of the ZnO thin films was estimated by plotting (*αhv*) 2 versus *hv*. As the *Ts* increases, the absorption edge of the doped film shifts to the shorter wavelength region (shown in Fig.3(a)) and the corresponding optical band gap slightly increases from 3.30 to 3.40eV (shown in Fig.3(b)). According to the theory of Burstein-Moss shift [Moszkowskrf S A, et al (1954) reported, Moss T S, et al (1954) reported], the variation of band gap (Δ*Eg*) is a function of carrier concentration (*n*) and it can be described as Δ*Eg*$\propto$ *Bn2/3* (*B* is a parameter containing the reduced effective mass). In this work, the carrier concentration (*n*) consequently varies from 2.28×1020 to 9.193×1020/cm3 upon a *Ts* promotion from RT to 250℃ (shown in Fig. 5), which is consistent with the theory of Burstein–Moss shift.

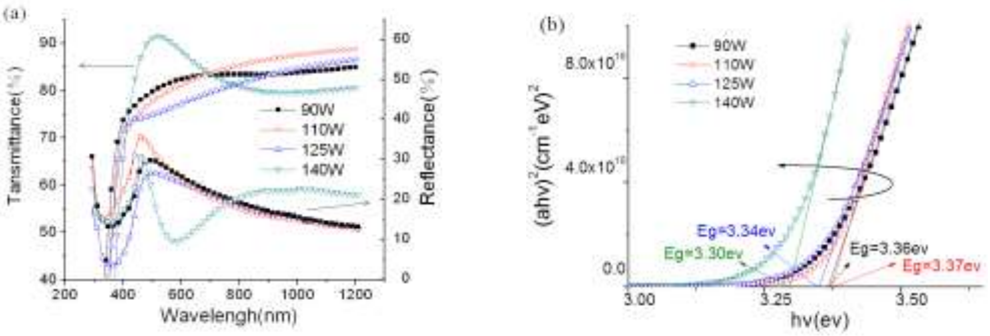

Figure 4: Optical properties of the AZO films with different Pw: (a) Transmittance and reflectance spectra of the as-deposited AZO films. (b) The corresponding dependence of (αhv) 2 on hv

3.4 Electrical properties

Fig. 5(a) exhibits the electrical properties of the AZO thin films deposited at different *Ts*. All the films exhibit *n*-type conductivity. The resistivity decreases rapidly with increasing *Ts*, which is attributed to an improved crystallinity with bigger crystal size and less defects in films. The XRD patterns in Fig.1 could be evidence. It is also found that annealing has strong effects on the further decreasing of electrical resistivity. Fig. 5(b) shows the electrical properties of the AZO films (AZO-1, AZO-2, AZO-3, AZO-4 and AZO-5) with annealing treatments. Carrier concentration (*n*) increases with a raising *Ts* and reaches a highest *n* of 9.193×1020/cm3 (*Ts*=250℃). However, the film's resistivity (*ρ*) decreases with an increasing *Ts*, and it drastically declines to the minimal *ρ* of 3.566×10-3 Ω·cm compared with the *ρ* of ~2×10-1 Ω·cm for the as-deposited counterpart (shown in Fig. 5(a)). Normally, the crystalline state of material is closely related to its resistivity. The resistivity has a reciprocal dependence on the mean free path of electron [Dai Daosheng, et al (1989) reported]. For an amorphous film, the mean free path is quite short due to its high defect density and atom disorder, thus leading to higher resistivity. High temperature, obtained by the annealing or through the substrate heating, contributes to the decrease of defect density as well as the atomic order configuration with little grain boundaries, and the possibility of the moving electrons being scattered would be reduced, the resistivity could thus be declined. For this reason, the 400℃-annealed AZO films (AZO-4, AZO-6, AZO-7, AZO-8 and AZO-9) were also selected to study the effects of the *Pw* on film's electrical properties. The *ρ* decreases with the *Pw* increasing from 70 to 110W, approaching the minimum at 110W, and then it increases with an increasing *Pw*. However, very high *Pw* causes a negative influence. When the *Pw* is increased to 140 W, the resistivity increased drastically, which is consistent with the literature's reports [Chang J F, et al (2000) reported, Dengyuan Song, et al (2002) reported].

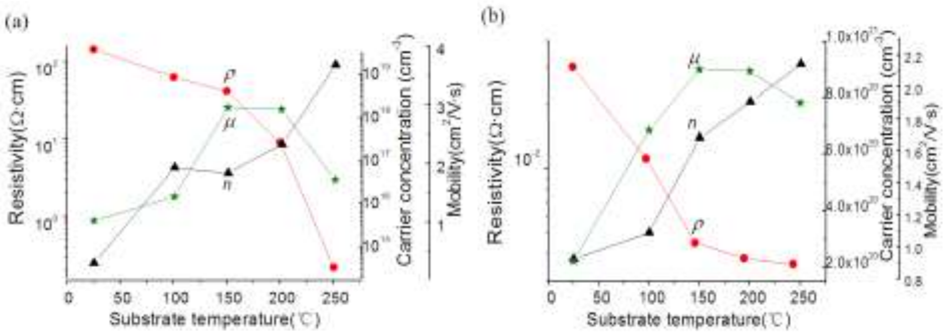

Figure 5: Influence of substrate temperatures on the electrical properties of the AZO thin films: (a) without annealing, (b) with annealing.

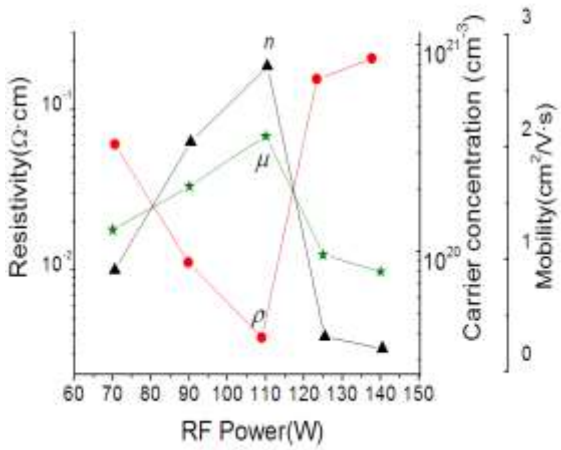

Figure 6: Electrical properties of the annealed AZO films deposited with different RF power

4. Conclusions

AZO thin films were deposited on glass substrates by RF reactive sputtering with a Zn-Al alloy target. Sputtering power, substrate temperature and annealing treatment have strong effects on the electrical and optical properties of the AZO films. High-quality AZO thin films with a preferential c-axis orientation can be obtained with a high substrate temperature (>150°C). The transmittance of the AZO thin films is more than 80% in visible light region, with the optical band gap of ~3.3eV. Annealing contributes to the further decreasing of electrical resistivity from ~2×10-1 to 3.566×10-3 Ω·cm. The AZO thin films with high transmittance (>80% in visible light region) and low electrical resistivity (~3×10-3 Ω·cm) could be prepared with the optimized parameters (*Ts*=250 °C, *Pw*=110W and 400 °C-annealing for one hour)

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