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Effect of annealing treatment on the structural, optical, and electrical properties of Al-doped ZnO thin films

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Abstract: Highly conductive and transparent Al-doped ZnO (AZO) thin films were prepared from a zinc target containing Al (1.5 wt.%) by direct current (DC) and radio frequency (RF) reactive magnetron sputtering. The structural, optical, and electrical properties of AZO films as-deposited and submitted to annealing treatment (at 300 and 400°C, respectively) were characterized using various techniques. The experimental results show that the properties of AZO thin films can be further improved by annealing treatment. The crystallinity of ZnO films improves after annealing treatment. The transmittances of the AZO thin films prepared by DC and RF reactive magnetron sputtering are up to 80% and 85% in the visible region, respectively. The electrical resistivity of AZO thin films prepared by DC reactive magnetron sputtering can be as low as 8.06×10^{-4} Ω·cm after annealing treatment. It was also found that AZO thin films prepared by RF reactive magnetron sputtering have better structural and optical properties than that prepared by DC reactive magnetron sputtering.

Key words: AZO thin films; structure; optical and electrical properties; annealing; transmittance spectra; electrical resistivity

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1. Introduction

AZO transparent conductive films are a kind of outstanding functional materials in the electrical and optical application fields. The high electrical conductivity and simultaneously high transparency in the visible wavelength range have attracted considerable attention in scientific research and in technological applications such as transparent electrodes, light-emitting diodes (LEDs), laser diodes (LDs), and solar energy cells [1-10]. To prepare high quality AZO thin films for application, it is important to analyze the structural and optical properties of AZO thin films. Although various experimental studies have been conducted on the synthesis of AZO thin films [11-21], some fundamental issues of the optical and electrical properties need further investigation.

Annealing is an effective posterior treatment to improve the properties of films. Generally, the properties of annealed films are related to the annealing temperature, time, and atmosphere. In this study, AZO thin films were prepared by DC and RF reactive magnetron sputtering, respectively, and the structural, optical, and electrical properties of as-deposited and annealed AZO films were investi-

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gated.

2. Experimental

AZO thin films were deposited on glass substrate using direct-current (DC) and radio-frequency (RF) reactive magnetron sputtering, respectively. The substrates were carefully cleaned in acetone, rinsed in alcohol, and then dried in hot air just prior to the deposition to improve the deposited adhesion to the substrates. The target was zinc containing Al (1.5 wt.%) with a diameter of 60 mm and a thickness of 5 mm. A pre-sputtering process was employed for 10 min to clean the target surface. A thermocouple was positioned on the substrate holder to control the substrate temperature during the growth of the film. O_2 was used as reactive species while Ar was used as sputtering gas. These were mixed in the sputtering chamber and their partial pressure was regulated by two mass flow controllers. The radio frequency reactive magnetron sputtering was carried out in mixed gas, applying radio frequency power of about 95 W with frequency at 13.56 MHZ. The deposition parameters are summarized in Table 1.

Table 1. Deposition conditions of AZO by DC and RF reactive magnetron sputtering

Parameter	DC	RF
Base vacuum / Pa	6.6×10^{-4}	6.0×10^{-4}
Working gas pressure / Pa	5	0.5
Sputtering power / W	60-80	95
Sputtering gas	Ar	Ar
Reactive gas	O_2	O_2
Deposition temperature / °C	200	200
Deposition time / min	45	45
Target-substrate distance / cm	8.5	5

As for the annealing treatment, the AZO thin films were sent to a quartz furnace in nitrogen gas at 300 and 400°C for 1 h, respectively. Crystallization of the AZO films were measured by an X-ray diffractometer with Cu K_α radiation (λ = 0.154056 nm). The surface morphology was characterized by atomic force microscopy (AFM. STM.PC-208B.C). Optical transmittance measurements were carried out using a UV-Vis spectrophotometer. The transmittance was automatically calibrated against a bare glass as a reference sample. The electrical resistivity, Hall mobility, and carrier concentration were determined from the Hall effect measurement equipment using van der Pauw method.

3. Results and discussion

3.1. Surface morphology and structural properties of AZO thin films

The typical AFM images of AZO films (flux ratio O_2/Ar = 0.3/27) prepared by DC reactive magnetron sputtering before and after annealing at 400°C in N_2 are shown in Fig. 1.

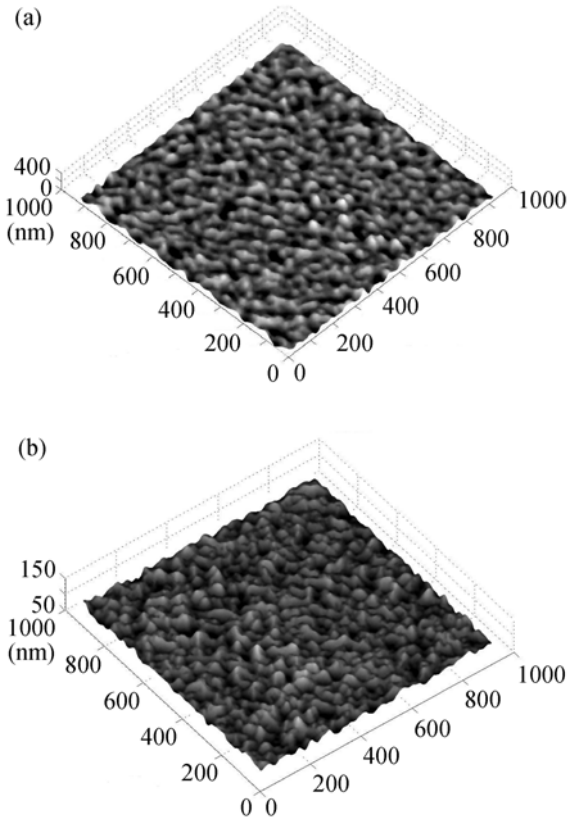

Fig. 1. AFM images of AZO thin films prepared by DC reactive magnetron sputtering: (a) as-deposited; (b) annealed at 400°C.

The scanning areas are 10 nm × 10 nm and 3.5 nm × 3.5 nm, respectively. The annealed films exhibit densely packed columnar crystalline grains with no visible pores and larger interface defects, as well as smoother surface. The surface roughness reduces after the annealing treatment.

The X-ray diffraction patterns of AZO thin films prepared by DC (O_2/Ar = 0.3/27) and RF reactive magnetron sputtering (O_2/Ar = 0.3/29) before and after annealing treatment in N_2 are shown in Fig. 2.

Both (002) and weak (101) peaks from the as-deposited AZO thin films prepared by DC reactive magnetron sputtering can be identified. The (002) peak is stronger, which indicates a preferential (002) *c*-axis orientation. When the AZO thin films were annealed in N_2 atmosphere, the intensity of (101) peaks decreased gradually and disappeared completely after annealing at 400°C. It demonstrates that the annealing treatment made the AZO thin films have more preferential orientation in the *c*-axis direction [22]. Meanwhile, with the annealing temperature increasing, the crystallization was enhanced. A strong (002) peak and a very weak (004) peak can be identified in the as-deposited AZO thin films prepared by RF reactive sputtering, indicating a polycrystalline structure with a preferential *c*-axis orientation. After annealing treatment, only the (002) peak was detected. Moreover, the as-deposited AZO thin films prepared by DC and RF reactive magnetron sputtering are highly oriented; however, the crystallization quality of AZO thin films prepared by RF is better than that prepared by DC reactive magnetron sputtering. The corresponding parameters of the (002) peak are listed in Table 2.

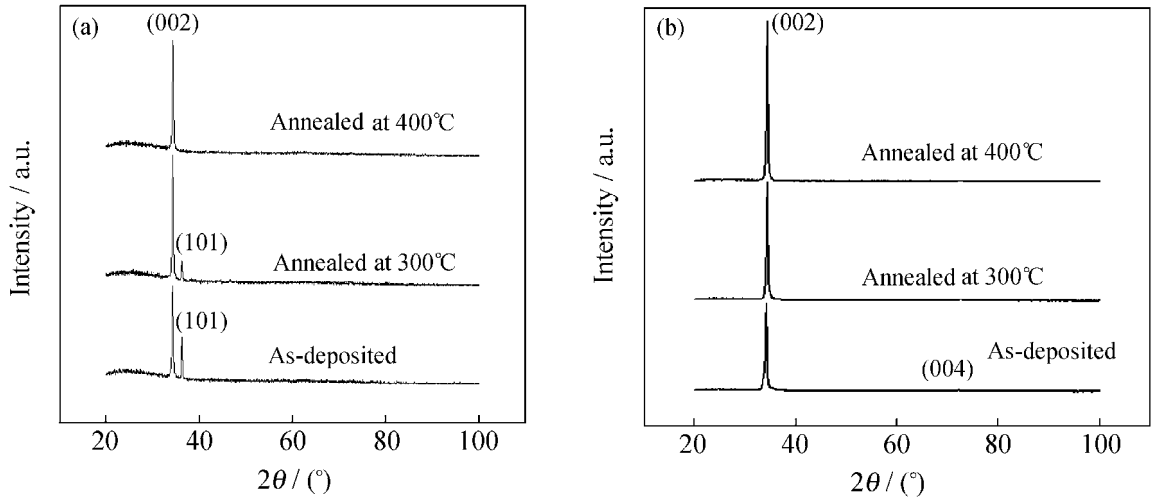

Fig. 2. X-ray diffraction patterns of AZO thin films before and after annealing: (a) DC; (b) RF.

Table 2. Parameters of the X-ray diffraction patterns of AZO films

Sample	2θ / (°)	FWHM / (°)	d_{hkl} / nm	c / nm	D / nm
As-deposited, DC	34.2397	0.29470	0.261676	0.523352	28.21
300°C, DC	34.2757	0.29220	0.261410	0.522820	28.45
400°C, DC	34.3218	0.29150	0.261069	0.522138	28.52
As-deposited, RF	34.2176	0.30880	0.261840	0.523680	26.92
300°C, RF	34.3711	0.29580	0.260706	0.521412	28.11
400°C, RF	34.3824	0.27970	0.260623	0.521246	29.73

Based on the XRD results, the average size (D) of the crystalline grains along the *c*-axis can be evaluated by Scherrer formula as follows [23]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where D is the grain size, λ is the X-ray wavelength (0.154056 nm), θ is the Bragg angle, and β is the full width at half maximum (FWHM) of the AZO (002) diffraction peak. The calculation results are presented in Table 2. With the increase of the annealing temperature, the grain size of the AZO thin films prepared by DC and RF reactive magnetron sputtering increase and the crystalline quality improves since annealing provides sufficient energy

for atom rearrangement. According to the Bragg formula: $\lambda = 2d\sin\theta$, where d denotes the crystalline plane distance for indices (*hkl*) and θ is the diffraction angle of the (002) peak. It can be understood that the decrease of the crystalline plane distance will result in the increase of the diffraction angle. From Table 2, it can be found that d decreases with increasing diffraction angle. This coincides with the theoretical results. It was found that all d values are larger than that of standard ZnO powder d_0, which is equal to 0.2603 nm. The annealing treatment of AZO thin films leads to a decrease in d values, but is still larger than that of the standard ZnO powder. The lattice constants c can be calculated by the following formula [24]:

$$d_{hkl}^{\ 2} = \left[\frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2}\right]^{-1} \quad (2)$$

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

3.2. Optical properties

Fig. 3 shows the transmittance in the UV-Vis regions for AZO thin films prepared by DC (O_2/Ar = 0.3/27) and RF reactive magnetron sputtering (O_2/Ar = 0.3/29) before and after annealing in N_2 at 300 and 400°C.

The optical transmittance in visible regions exceeds 80%, but decreases substantially at short wavelengths near the ultraviolet range for all thin films. At wavelength λ = 300 nm, the transmittance is almost zero, which is attributed to the onset of fundamental absorption. Moreover, the absorption edge of the films was observed to shift slightly towards a shorter wavelength after annealing treatment. Annealing treatment has no significant influence on the transmittance in the visible region. The AZO thin films prepared by DC and RF reactive magnetron sputtering show average transmittance above 80% and 85% in the visible region, respectively. The higher transmittance suggests better crystallization. This is in good agreement with the XRD results, from which it can be concluded that the AZO thin films prepared by RF reactive magnetron sputtering had better crystallization than those prepared by DC reactive magnetron sputtering.

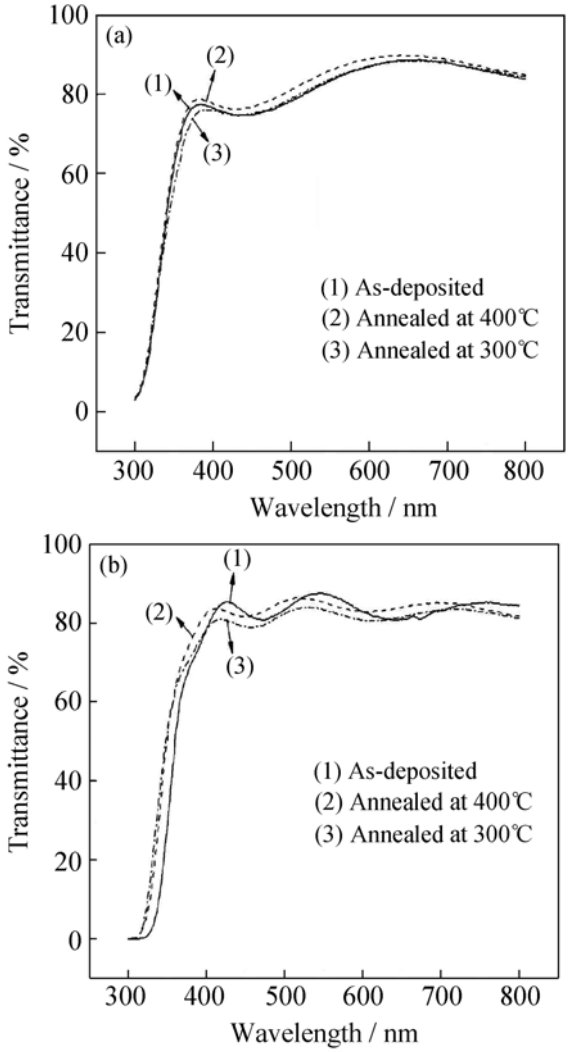

Fig. 3. Transmittance in the UV-Vis regions of AZO films before and after annealing: (a) DC; (b) RF.

For a direct band gap semiconductor, the optical absorption coefficient α that provides the information of the band structure is given by the following formula [25]:

$$I = I_0\exp(-\alpha d) \quad (3)$$

where I_0 and I denote the intensities of the incident light and the transmitted light, respectively, and d is the film thickness. For AZO with a direct band structure, $\alpha h\nu = (h\nu - E_{\text{opt}})^{1/2}$, where $h\nu$ is the photon energy and E_{opt} is the optical band gap. The optical band gap E_{opt} can be obtained by extrapolating the straight-line portion of $(\alpha h\nu)^2$ vs $h\nu$

plots to the energy axis [26-27]. The obtained optical band gaps were 3.47 and 3.37 eV for AZO thin films prepared by DC and RF reactive magnetron sputtering, respectively.

The optical absorption at the absorption edge corresponds to the transition from the valence band to the conduction band, while the absorption in the visible region is related to some local energy levels caused by some intrinsic defects. Thus, λ (nm) corresponding to the apparent optical absorption edge can be estimated by the relation: $\lambda = 1240.7 / E_{\text{opt}}$ (nm) [28]. By calculation, the sharp absorption edge of AZO thin films prepared by DC and RF reactive magnetron sputtering was approximately 358 and 368 nm, respectively.

3.3. Electrical properties

All transparent conducting AZO thin films have n-type conductivity. The high conductivity of these films results mainly from stoichiometric deviation. The conduction characteristics of ZnO are primarily dominated by electrons generated by the O^{2-} vacancy and Zn interstitial atoms [29].

The electrical conductivity in AZO film is higher than that in pure ZnO films because of the additional contribution from Al^{3+} ions on substitutional sites of Zn^{2+} ions and Al interstitial atoms. The electrical resistivity ρ, Hall mobility μ, and carrier concentration n of AZO thin films deposited by DC reactive magnetron sputtering at different annealing temperatures are summarized in Table 3.

Table 3. Electrical properties of AZO thin films before and after annealing treatment

Annealing temperature / °C	Resistivity / (Ω·cm)	Carrier concentration / (10^{20} cm^{-3})	Hall mobility / ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
As-deposited, DC	1.268×10^{-3}	3.4	14.27
300, DC	1.052×10^{-3}	3.6	16.5
400, DC	8.06×10^{-4}	4.0	19.3
As-deposited, RF	1.617	1.6	0.0238

It can be seen that the electrical resistivity of as-deposited AZO thin films prepared by DC reactive magnetron sputtering was 1.268×10^{-3} Ω·cm. However, after annealing treatment in N_2, the electrical resistivity decreased to a minimum of 8.06×10^{-4} Ω·cm at 400°C. From the relation: $\rho = 1/ne\mu$, this lower electrical resistivity of AZO thin films was caused by the higher product of the carrier concentration n and mobility μ. The increase of carrier concentration is attributed to the enhancement of the oxygen vacancy. High annealing temperature can enhance the mobility that can improve the porosity and quality of films since the crystallite size becomes larger and the crystallinity of the films improve with an increase in the annealing temperature. The increase in the mobility is in conformity with the improvement of the films' crystallinity.

However, good values of electrical resistivity, carrier concentration, and Hall mobility of the AZO thin films deposited by RF reactive magnetron sputtering cannot be obtained. The electrical resistivity and Hall mobility of the as-deposited sample were 1.617 Ω·cm and 0.0238 $cm^2/(V \cdot s)$, respectively. After annealing at 400°C, the electrical resistivity of the AZO thin films prepared by RF reactive magnetron sputtering decreased to 10^{-2} Ω·cm. Though the AZO thin films prepared by RF reactive magnetron have better crystallization and high transmittance, the electrical properties are less than those prepared by DC reactive magnetron sputtering. It depends on the film thickness and other preparation conditions.

All results shown above illustrate that the annealing treatment has a strong influence on the electrical properties of AZO thin films and that it is a good technique to improve the electrical conductivity of the as-deposited AZO thin films.

4. Conclusions

AZO thin films were deposited by DC and RF reactive magnetron sputtering and were annealed in N_2. The AFM images show that the surface of the annealed AZO thin films is relatively smooth. The grain sizes of the annealed sample are larger than

those of the as-deposited for the same sample. XRD analysis indicates that the AZO thin films are poly-crystallized but with a preferential orientation (002) along the *c*-axis. After annealing in N_2, the AZO thin films exhibit better *c*-axis orientation. The crystalline plane distance *d* decreases whereas the crystallite average size *D* increases with increasing annealing temperature. The AZO thin films prepared by RF reactive magnetron sputtering have better crystallization than those prepared by DC reactive magnetron sputtering. The transmittance of AZO thin films in the visible region increases with the annealing temperature. The AZO thin films prepared by DC and RF reactive magnetron sputtering show an average transmittance of above 80% and 85% in the visible region, respectively. With increasing annealing temperature, the electrical conductivity and the carrier concentration of the AZO thin films deposited by DC reactive magnetron sputtering increase. In a word, the annealing process leads to an improvement of the (002) orientation and an increased carrier concentration. High-quality AZO thin films can be obtained by annealing treatment.

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