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RESEARCH ARTICLE

Influence of process parameters on band gap of Al-doped ZnO film

Diqiu HUANG, Xiangbin ZENG (✉), Yajuan ZHENG, Xiaojin WANG, Yanyan YANG

School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

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Abstract This paper presents the influence of process parameters, such as argon (Ar) flow rate, sputtering power and substrate temperature on the band gap of Al-doped ZnO film, Al-doped ZnO thin films were fabricated by radio frequency (RF) magnetron sputtering technology and deposited on polyimide and glass substrates. Under different Ar flow rates varied from 30 to 70 sccm, the band gap of thin films were changed from 3.56 to 3.67 eV. As sputtering power ranged from 125 to 200 W, the band gap was varied from 3.28 to 3.82 eV; the band gap was between 3.41 and 3.88 eV as substrate temperature increases from 150°C to 300°C. Furthermore, the correlation between carrier concentration and band gap was investigated by HALL. These results demonstrate that the band gap of the Al-doped ZnO thin film can be adjusted by changing the Ar flow rate, sputtering power and substrate temperature, which can improve the performance of semiconductor devices related to Al-doped ZnO thin film.

Keywords Al-doped ZnO thin films, band gap, carrier concentration, argon (Ar) flow rate, sputtering power, substrate temperature

1 Introduction

Transparent conductive film (TCO) has been developed rapidly, and reached a climax in recent years due to the development of microelectronics, solar energy and other industries. TCO material is required with not only high optically transmittance (80%) in a wide range of wavelength (300–1000 nm), but also high conductivity, and the resistivity must be less than 1×10^{-3} Ω·cm [1,2]. Typical TCO materials include stannic oxide (SnO_2), indium oxide (In_2O_3), gold (Au), palladium (Pd) and zinc oxide (ZnO). However, Au and other metal films absorb too much light accompanied with a low hardness and poor stability, so they have been replaced by metal oxide (SnO_2, In_2O_3 and ZnO) transparent conductive oxide film gradually [3]. In particular, the most popular TCO, In_2O_3:Sn (ITO) is widely used in booming flat-panel displays, especially large-screen TV. However, there are potential troubles in the future application for the short supply of raw material (0.1 ppm of In_2O_3) and environmentally hazardous (In) [4,5]. Al doped ZnO (AZO) film has ever attracted considerable attention in the past three decades due to its unique combination of high transparency and low resistivity [6–8]. AZO film has many advantages over ITO films: abundant in raw materials (132 ppm of ZnO), non-toxic, more affordable, and similar property to ITO films. AZO is expected to be the alternative of ITO [9].

ZnO is a new type of II-VI semiconductor with wide and direct band gap (3.3 eV at room temperature). It belongs to hexagonal crystal system with a point group of 6 mm (Hermann-Mauguin notation) and space group C_{6v}^4 ($P6_3mc$) with high exciton binding energy (60 meV at room temperature and the thermal ionization is 26 meV) [10–14]. AZO has almost the same structure and properties as ZnO. In addition, the performance of AZO is more stable than that of ZnO. Therefore, AZO is expected to be applied to many devices, such as transparent electrodes, solar cell window materials, UV detector and optical waveguide devices [15–17].

However, it is essential to realize that the tuning of band gap before the AZO can be applied to light emitting devices. And it is also very important to tune the band gap of window layer (like AZO thin film) in solar cells to control the range of light absorption and improve its efficiency [5,6]. Previous researches indicated there is a certain relationship between band gap and carrier concentration [18–22]. And almost all of these researches can be classified in two main areas: one focuses on simulation algorithm (first-principles plate-wave pseudopotential method based on the density functional theory) to study

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E-mail: eexbzeng@163.com

the correlation between band gap and carrier concentration [18,20]; the other one emphasizes on the influence of element [21,22] or content [22–24] of dopant on the band gap by experiments. However, few researches pay attention to the influence of process parameters (especially for magnetron sputtering method) on the band gap of AZO thin films, which can provide scientific and theoretic evidence to tune the band gap of AZO in the experimental procedure. This study aims to examine the influence of process parameters on the band gap of the AZO film, which might be helpful to further study the correlation between band gaps and carrier concentration. In the experiments, process parameters includes the argon (Ar) flow rate, sputtering power and substrate temperature, these parameters were changed in this study and accordingly carrier concentration were altered, and then the changes of band gap of AZO thin films were investigated.

2 Method

2.1 Theory and calculations

There is a theoretical formula to calculate the band gap E_g. The E_g can be described by the following equations from Eqs. (1) to (3) [20,25,26].

$$E_g = E_o + \Delta E_{BM} - \Delta E_g, \tag{1}$$

$$\Delta E_{BM} = (h^2/8m^*)(3/\pi)^{\frac{2}{3}}N^{\frac{2}{3}}, \tag{2}$$

$$\Delta E_g = (e/2\pi\varepsilon_0\varepsilon_1)(3/\pi)^{\frac{1}{3}}N^{\frac{1}{3}}, \tag{3}$$

where E_g means the band gap of the film, E_o is the bang gap of single crystal ZnO, ΔE_{BM} means the expansion of band-gap due to the Burstein–Moss effect [27]. Burstein-Moss effect is the process that the band gap of a semiconductor is expanded as the absorption edge is pushed to higher energies as a result of all states close to the conduction band being populated. The effect occurs when the carrier concentration exceeds conduction band edge density of states, which corresponds to degenerate doping in semiconductors. That is to say, when the degeneracy occurs in the semiconductor, Fermi level will go up into the conduction band, which can expand the band gap. ΔE_g represents the contraction of band gap caused by carrier scattering and ionized impurities, h is Plank's constant, m^* is the effective mass of carrier, N is carrier concentration, which is the only factor for changing the band gap.

To obtain the band gap of AZO film, the transmission was measured first. Then the transmission was translated into the absorption spectra by the Kubelka-Munk method [28] in Eq. (4).

$$\alpha = -\frac{\ln T}{d}, \tag{4}$$

where α is the absorption coefficient of film, T means transmittance, d is the thickness of film.

Then, the band gap of AZO films can be obtained by extrapolating the linear portion of the square of absorption coefficient α against photon energy $h\nu$ using the Tauc (Eq. (5)) [23].

$$(\alpha h\nu)^2 = A(h\nu - E_g). \tag{5}$$

After obtaining the curve about $(\alpha h\nu)^2 \sim h\nu$ and drawing the tangent of its linear part, the intersection of the tangent and the horizontal axis is the value of band gap.

2.2 Experiments

The experimental method used for the preparation of AZO thin films was radio frequency (RF) magnetron sputtering. The sintered ceramic AZO disk containing 3 wt% Al_2O_3 with a size of $\Phi 100 \times 5$ mm was used as sputtering target, placed paralleling to the target surface with a 60 mm distance. Pure Ar gas was introduced into the chamber at a base pressure of 3.5×10^{-3} Pa. Figure 1 shows the experimental procedure. More detail about the three process parameters in experiments are shown in Table 1.

The transmittance of the AZO films was examined by

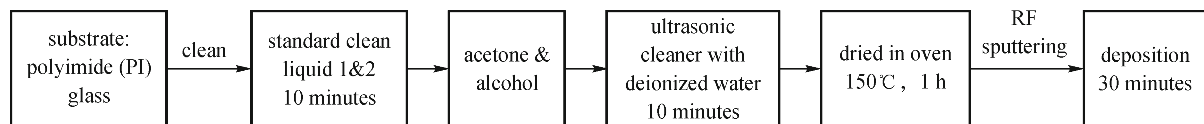

Fig. 1 Experimental procedure

Table 1 Deposition parameters

parameters	details				
Ar flow rate/sccm*	30	40	50	60	70
RF power/W	100	125	150	175	200
substrate temperature/°C	150	200	250	300	350

Note: * sccm is the abbreviation of state cubic centimeter per minute

UV visible spectrophotometer (UV-2550) in the wavelength of 200–1000 nm. The structural properties analyzed with X-ray diffraction (XRD, X'Pert PRO) were carried out at room temperature (25°C). All the available reflections were recorded with the angle 2θ from 10° to 90°, and the step size is 0.0170°. The alignment of the diffractometer was verified by a silicon sample. The AZO film thickness was measured by α-step method (KLA TENCOR P16 +). Carrier density was examined by HALL measuring instrument (Lake Shore 7704), and scanning electron microscope (SEM) image was obtained by SEM Sirion 200.

3 Results and discussion

3.1 Effect of Ar flow rate on band gap of AZO film

Figure 2(a) shows the changes of the transmittance of PI and AZO film deposited under different Ar flow rate with the wavelength of incident light in the visible region. And the shift of absorption edge can be observed in Fig. 2(b).

As shown in Fig. 2(a), AZO film has a steep cutoff absorption limit, the optical transmission spectra exhibit a transmittance around 80% in the visible region. Figure 2(b) displays the transmittance spectrum from 300 to 400 nm, and it was found that the redshift occurs, when the Ar flow rate is increased from 30 to 70 sccm. This phenomenon is mainly due to Burstein-Moss effect.

To observe the variation of band gap qualitatively, the values of band gap can be obtained directly via Eqs. (4) and 5 by the graphical methods as mentioned in Section 2.1.

Figure 3(a) shows the changes of $(\alpha h\nu)^2$ as a function of photon energy with the variation of Ar flow rate of the AZO thin films. The band gap E_g can be evaluated from the interception of the extrapolated linear part of the curve with the photon energy axis. And the changes the band gap with Ar flow rate in representative experiments were shown in Fig. 3(b), in which the curve 1 is based on the result data indicated in Fig. 3(a), and the other two curves are derived from other two experimental results. The band gap decreased from 3.67 to 3.56 eV when the Ar flow rate increased from 30 to 70 sccm.

The band gap was obtained by transmittance. The working pressure can affect the transmittance. It has been reported that the working pressure increased as the Ar flow rate increases [25]. When the pressure increases to a certain value, the sputtering atoms will have enough kinetic energy, and the collisions between sputtering atoms, molecules and ion will increase. Then surface roughness will increase due to porous and columnar film structure caused by defects. And the rough surface will scatter the incident light, resulting in lower transmittance, which will contribute to the decreased band gap. To investigate whether working pressure influence the bandgap, a XRD test carried out on AZO films. The changes of full width at half maximum (FWHM) with different Ar flow rate were also examined.

Figure 4 (a) is XRD spectra results, and this XRD spectra shows that the lower the FWHM, the better the structure property of thin film. From Fig. 4(b), the FWHM has an irregular correlation with Ar flow rate. It means the working pressure is not effective enough to force the sputtered gas molecules into film, which will damage the crystal structure. Because if there are gases pockets in the thin film resulting from the pressure, the number of the gas pocket will increase with pressure, leading to worsen the properties of film. Therefore, it is not the working pressure affects the transmittance, but the carrier concentration. To

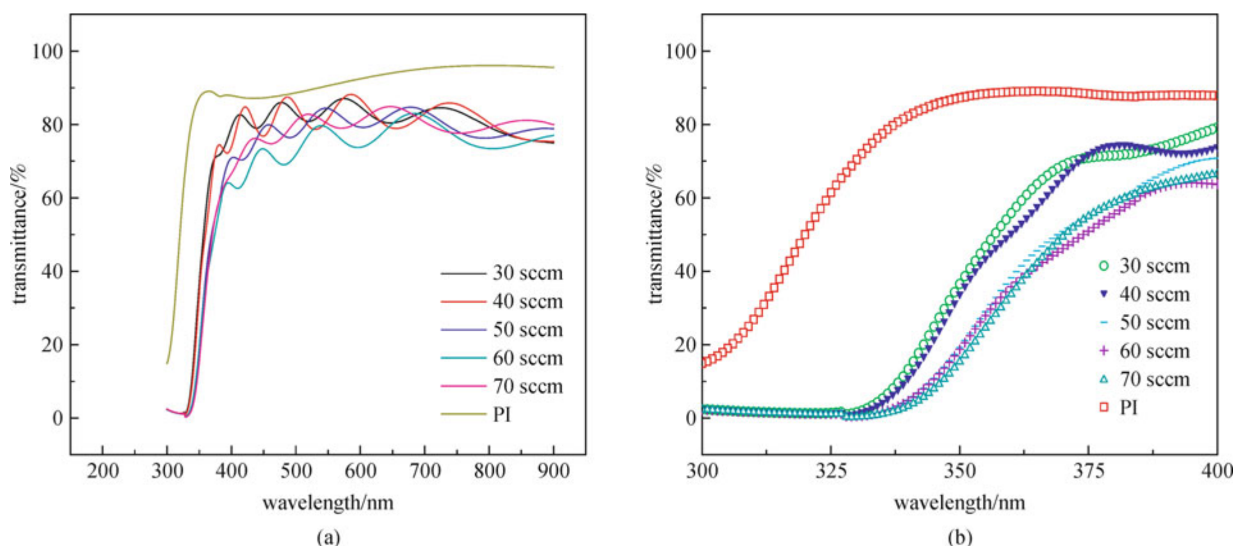

Fig. 2 (a) Transmittance with different Ar flow rate; (b) transmittance spectrum from 300 to 400 nm

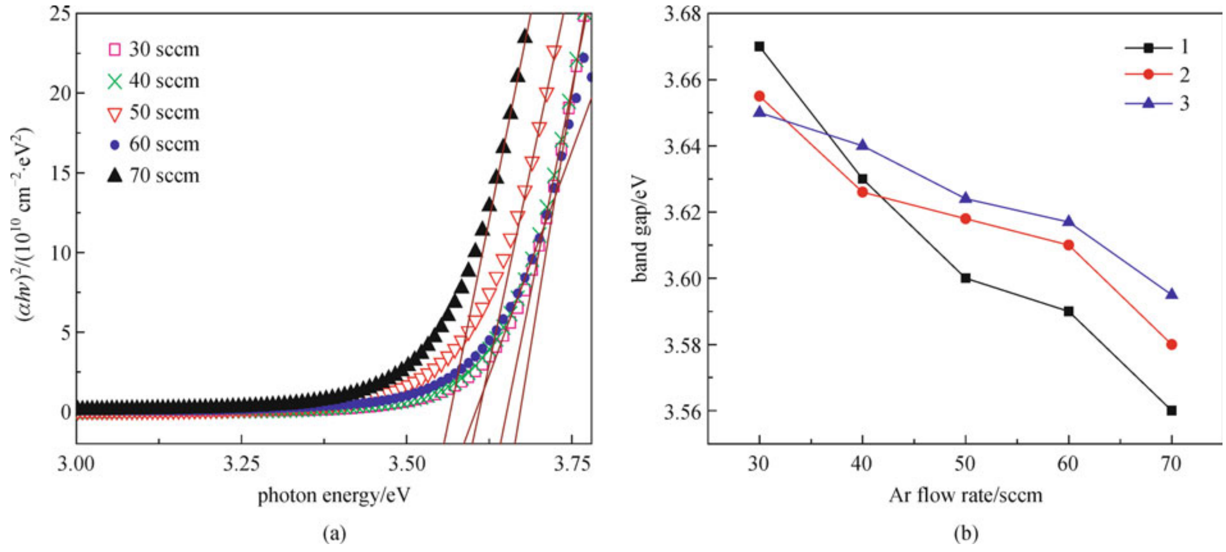

Fig. 3 (a) Plot of $(\alpha h\nu)^2$ versus photon energy for AZO films with different Ar flow rate; (b) band gap with different Ar flow rate

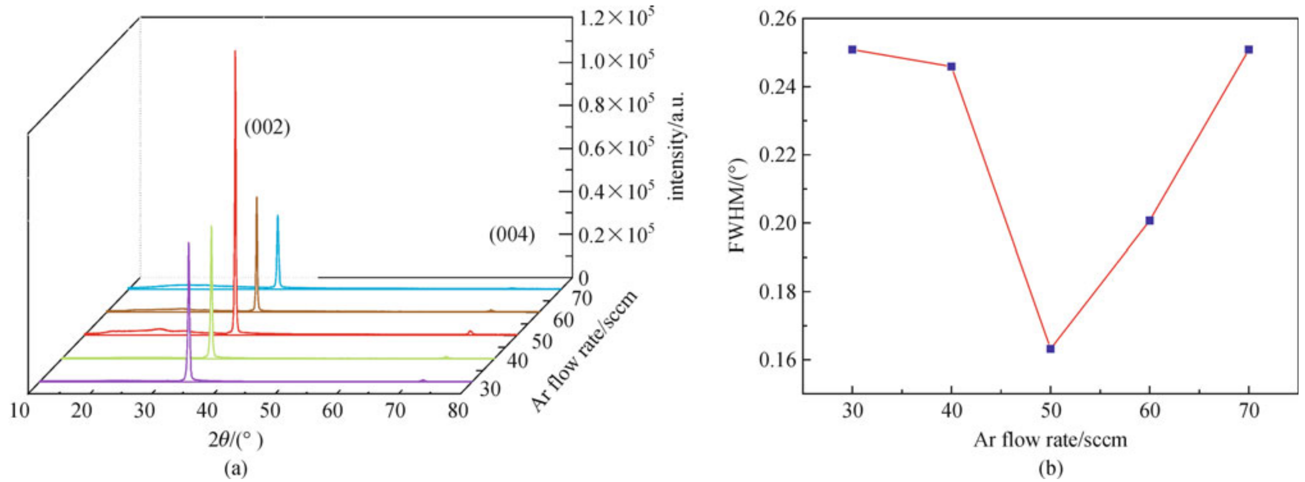

Fig. 4 (a) XRD spectra; (b) FWHM with different Ar flow rate

examine the relationship between carrier concentration and Ar flow rate, it is necessary to perform further study.

Based on kinetic theory of gases, there is a certain relationship between average free path of gas molecules and pressure based on Eq. (6) [25,29].

$$\bar{\lambda} = \frac{kT}{\sqrt{2}\pi p d^2}, \tag{6}$$

where $\bar{\lambda}$ is the average free path of gas molecules, k denotes Boltzmann constant, T means the temperature of gas, d denotes diameter of gas molecules, p is the pressure. In this formula, when d and T are constant, if p increases, $\bar{\lambda}$ will decrease. It means that the collision probability of gas molecules will increase.

In this experiment, as the Ar flow rate increases, the pressure in chamber increases, so that the collision probability between sputtered atom and Ar molecule increases. On the other hand, the probability of sputtered atoms back reflection and scattering from gas molecules will increase. All of these will lead to huge energy loss of sputtered atoms, resulting in reduction of sputtered atoms which should reach the substrate. Then the carrier concentration in the deposited film will decrease, resulting in a reduction in band gap.

3.2 Effect of sputtering power on band gap of AZO film

In this section, AZO films were deposited on PI substrate with different power. Figure 5 are SEM images of AZO thin film samples deposited with different power. It can be seen that the effect of the sputtering power on the film morphology is significant. The AZO grain size increase from 20 to 45 nm with increasing power (125–200 W),

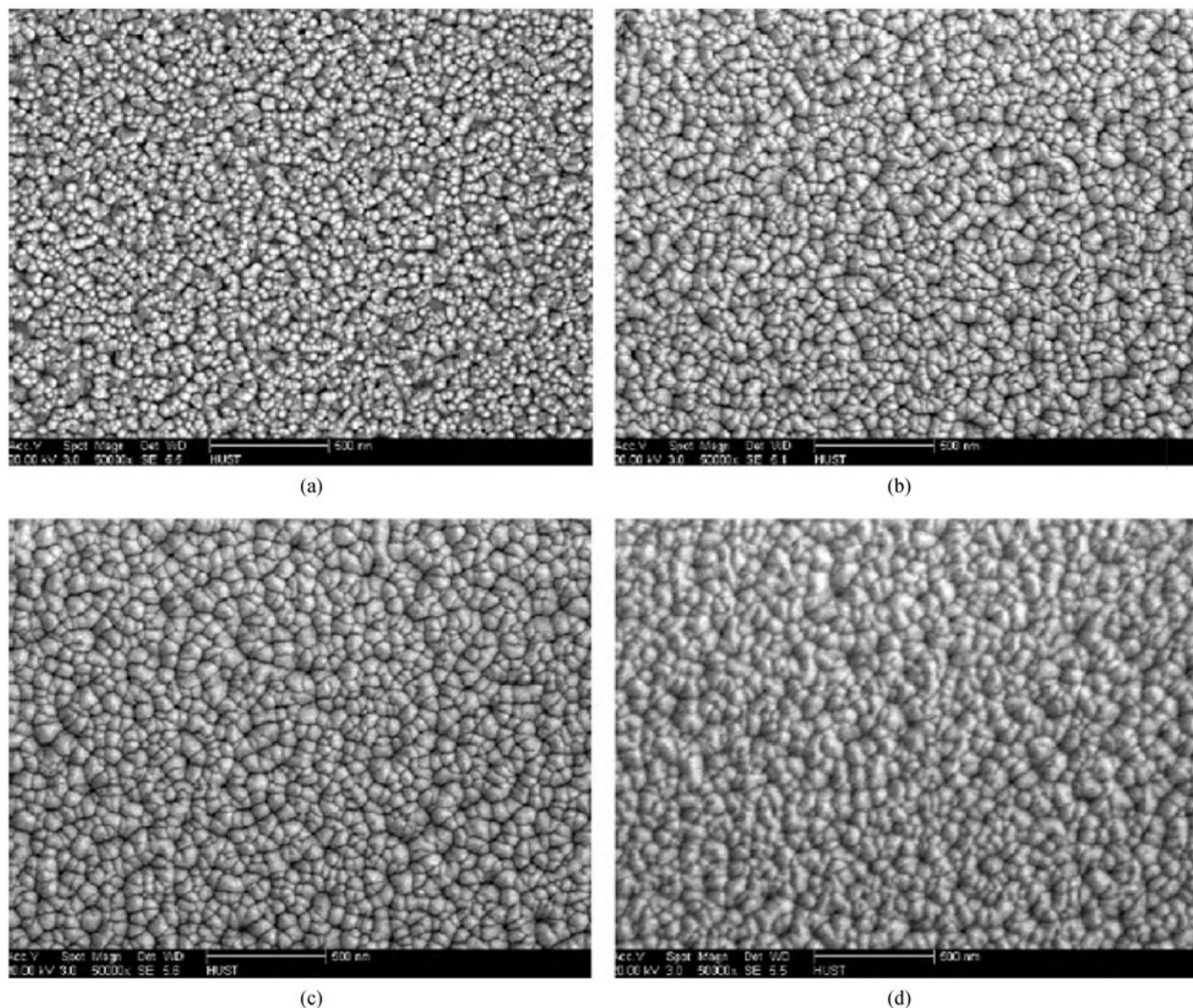

Fig. 5 SEM images with different power (a) 125 W; (b) 150 W; (c) 175 W; (d) 200 W

which is conducive to the transmittance.

The calculations were repeated as the former section. The transmittance-wavelength curves are depicted in Fig. 6 (a), the band gap was shown in Fig. 6(b), and the changes of carrier concentration are presented in Fig. 6(b) as well.

As shown in Fig. 6(b), when the RF power increases from 100 to 200 W, the band gap increases from 3.31 to 3.82 eV, at the same time, the carrier concentration linearly increase with power. The detailed results are given in Table 2, experiment 1 is the result which was presented in Fig. 6 (b), and the experiment 2 and 3 are another two experimental results. These results indicate that the band gap is proportional to the concentration, which is consistent with the theoretical formula. The possible reason is when power increases, the kinetic energy of sputtered Zn, Al and O atoms increases contributing to lateral movement on the substrate surface, which is helpful for the increase of carrier concentration, so that the band gap is expanded.

3.3 Effect of substrate temperature on band gap of AZO film

Considering the temperature tolerance of PI substrate, AZO films were deposited on glass substrate with different substrate temperatures. Figure 7(a) shows the transmittance of AZO films with different substrate temperature. The changes of band gap and carrier concentration are shown in Fig. 7(b).

In Fig. 7(b), the change of band gap is consistent with the carrier concentration variation. When the substrate temperature increases from 150°C to 300°C, the carrier concentration and the band gap both increase with the augment of substrate temperature. It is likely explained that the higher substrate temperature provide more energy to deposition atoms to enhance mobility, resulting in decrease of defects in the AZO films. On the other hand, higher substrate temperature is favorable to desorption of oxygen atoms in the film, which can reduce the concentration of

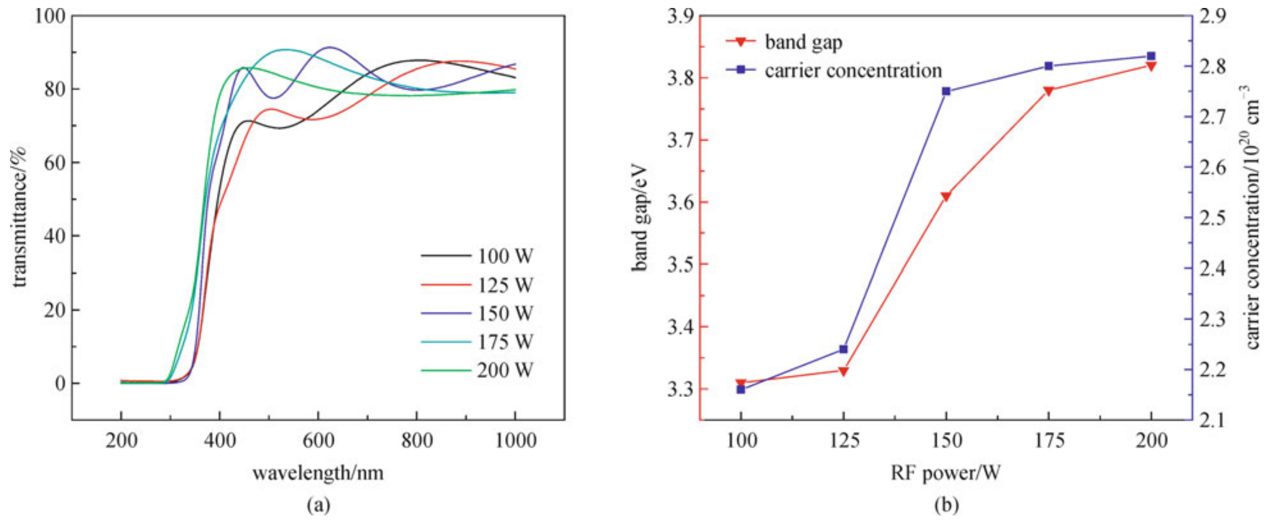

Fig. 6 (a) Transmittance with different power; (b) band gap and carrier concentration with different power

Table 2 Experimental results of band gap and carrier concentration with different sputtering power

RF power/W	experiment 1		experiment 2		experiment 3	
	$N/10^{20}$ cm^{-3}	E_g/eV	$N/10^{20}$ cm^{-3}	E_g /eV	$N/10^{20}$ cm^{-3}	E_g /eV
100	2.16	3.31	2.20	3.28	2.23	3.33
125	2.24	3.33	2.22	3.30	2.30	3.34
150	2.75	3.61	2.68	3.55	2.73	3.57
175	2.8	3.78	2.76	3.70	2.81	3.71
200	2.82	3.82	2.79	3.77	2.86	3.80

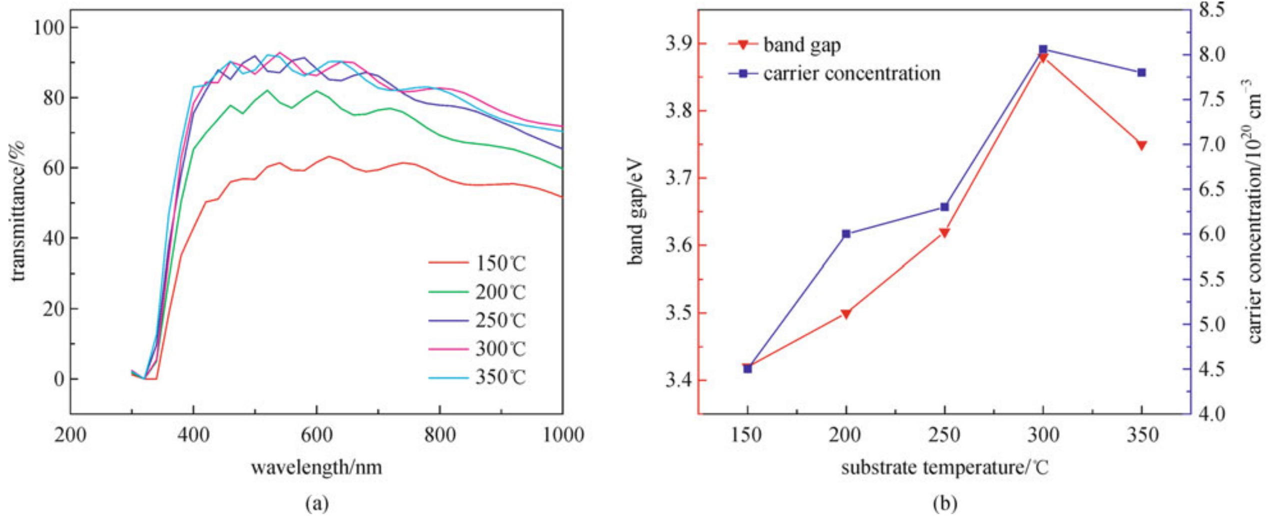

Fig. 7 (a) Transmittance, (b) band gap and carrier concentration with different substrate temperatures

electron traps. Therefore, the carrier concentration increased as described above. However, when the temperature increased to 350°C, more and more Al atoms were oxidized to Al_2O_3 (alumina), leading to a reduction of carrier concentration, so that the band gap declined. This suggests the band gap can be modulated from 3.42 to 3.88 eV by changing the substrate temperature from 150°C to 300°C.

4 Conclusions

Band gap is a key factor in the application on both light emitting devices and thin film solar cells, which determines

the performance of these semiconductor devices.

The effects of Ar flow rate, sputtering power and substrate temperature on band gap of AZO thin film were studied in this paper. Under different Ar flow rates varied from 30 to 70 sccm, the band gap of thin films were changed from 3.56 to 3.67 eV; As sputtering power ranged from 125 to 200 W, the band gap was varied from 3.28 to 3.82 eV; the band gap was between 3.41 and 3.88 eV as substrate temperature increased from 150°C to 300°C. At the same time, the carrier concentration was measured by HALL, it was found that the band gap was proportional to carrier concentration in a certain range. These results demonstrate that the band gap of the AZO thin film can be adjusted by the changes of Ar flow, sputtering power and substrate temperature, which can improve the performance of semiconductor devices related to AZO thin film.

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