Structural, Electrical, and Optical Properties of Transparent Conductive Al-Doped ZnO Films Prepared by RF Magnetron Sputtering

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Abstract: Highly conductive transparent Al-doped zinc oxide (AZO) films with highly (002)-preferred orientation were successfully deposited on glass substrates at room temperature by RF magnetron sputtering. Optimization of deposition parameters was based on sputtering RF power and Ar pressure in the vacuum chamber. AZO films of 180nm with an electrical resistivity as low as $2.68 \times 10^{-3} \ \Omega \cdot$ cm and an average optical transmission of 90% in the visible range were obtained at RF power of 250W and Ar pressure of 1.2Pa. The effect of chemisorption of oxygen on the grain boundary would capture electrons from conduction band and lead the formation of potential barriers among the crystallites, which will influence the electric property of the AZO thin films. The films have satisfactory properties of low resistance and high transmittance for application as transparent conductive electrodes in light emitting diodes (LEDs) and solar cells.

Key words: RF magnetron sputtering; transparent conductive film; AZO film
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1 Introduction

Recently, a great deal of interest has been fueled in zinc oxide (ZnO) semiconductor materials. They are transparent at visible wavelengths, have direct and wide bandgap ($E_g \approx 3.30$eV at room temperature), and have a large exciton binding energy (~ 60meV at room temperature). Such properties make them well suited for many optoelectronic applications including transparent conductive oxides in display devices and solar cells[1,2]. Doped ZnO has similar electrical and optical properties to ITO, but it is a nontoxic material, which has high temperature stability and costs less to manufacture[3]. Recent research demonstrated that using B, Al, Ga, In, and F as dopants resulted in ZnO films with low resistivity and high transmittance in the visible region[4~9].

Different technologies, such as electron beam evaporation[10], sol-gel[11], chemical spray[12], pulsed laser deposition[13], and DC and RF magnetron sputtering[14,15], have been used to prepare thin films of Al-doped zinc oxide (AZO) with adequate performance for applications. The RF magnetron sputtering technique has some advantages in comparison to the other methods. This technique is quite simple and the required setup is less expensive, and it is considered to be the most available deposition method to obtain highly uniform films with high packing density and strong adhesion at a high deposition rate. However, most researches have reported the AZO films deposited by magnetron sputtering on high temperature substrate, such as 250℃ glass[14~16]. The high temperature (more than 150℃) will destroy the active performance of photoresist, leading to invalidation of lift off, which is broadly utilized in semiconductor fabrication process. In order to being compatible to the lift off technology in semiconductor fabrication process, researches for AZO films deposition technology at low temperature are necessary. In this paper, AZO films are grown by RF magnetron sputtering at low temperature, and the structural, electrical, and optical properties of the AZO thin films with different deposition conditions are studied in detail.

2 Experiment

The AZO films were deposited on glass substrates in a conventional JS3X-100B RF magnetron sputtering system with a base pressure of 6×10^{-4}Pa at room temperature. A sintered ceramic sputter target with a mixture of ZnO (99.99% purity) and Al_2O_3 (99.99% purity) was employed as source material. The content of Al_2O_3 added to the sputter target was 2% in weight. The distance between sputter target and substrate is about 8cm. The sputtering power and Ar pressure were varied from 50 to 300W, and from 0.1 to 2.0Pa respectively. The sputtering time was varied
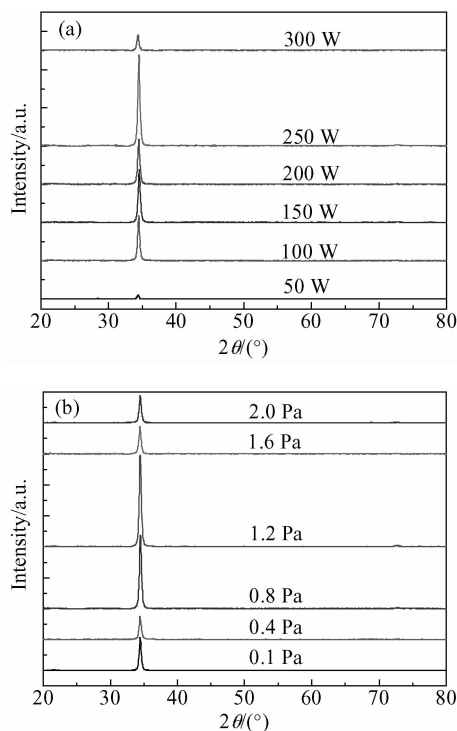
Fig. 1 X-ray diffraction patterns of AZO films deposited under different powers（a）and different pressures（b）

from 6 to 30min，corresponding to the thickness varied from 180 to 900nm with appropriate power and pressure. The structural properties of AZO films were analyzed with a Panalytical X´pert PRO powder X-ray diffractometer that uses Cu as radiation（$\lambda = 0.15406$nm）. The surface morphology of AZO films was examined using an SPA-400 atomic force microscope（AFM）. The optical transmittance of AZO films was measured using a Cary5000 spectrophotometer. The film thickness was determined using a Dektak3 surface profile measurement system. The sheet resistance，the carrier concentration and carrier mobility of AZO films were measured using Accent HL5500 Hall System with a four-point probe at room temperature.

3 Results and discussion

3.1 Structural properties

XRD patterns of the films grown on glass at different sputtering powers and Ar pressures are shown in Fig. 1. The AZO films were 180nm thick. Only the Bragg reflections which correspond to the ZnO（002）planes（$34.38° \sim 34.53°$）appear，indicating that the films are c-axis oriented. The highest value of the XRD test was obtained from the AZO thin films deposited at power of 250W and Ar partial pressure of 1.2Pa，as shown in Fig. 1，implying that the AZO thin films have the greatest multi-crystal structure. To as-
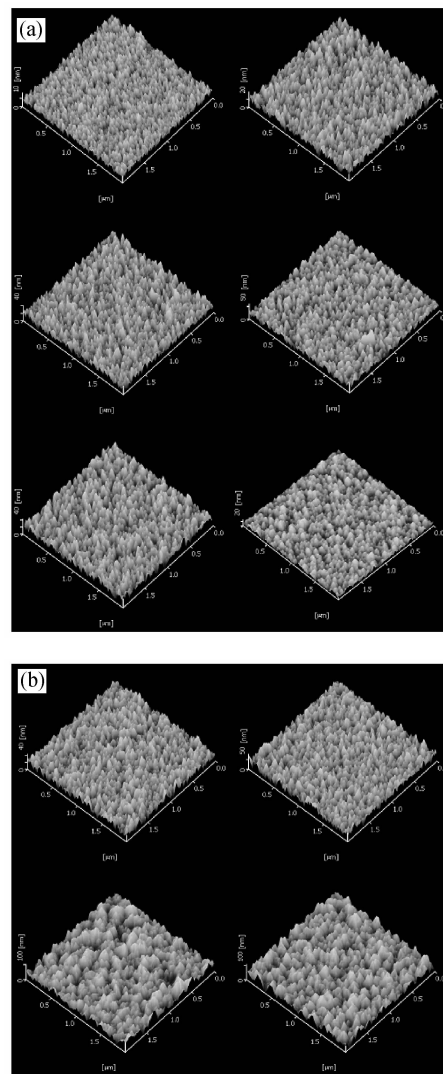

Fig. 2 Atomic force microscopic images of the film surface（scan size $2\mu m \times 2\mu m$）for various growth （a）Sputtering power：from 50 to 300W；（b）Sputtering time：from 12 to 30min

sess the quality of the AZO films，the full-width at half-maximum（FWHM）values of（002）peak and the crystallite dimension estimated are used according to Scherrer formula. The FWHM values of AZO vary from 0.334 to 0.363，exhibiting good crystallinity. No Al_2O_3 phase was found，impling that Al atoms substitute Zn in the hexagonal lattice and Al ions may occupy the interstitial sites of ZnO or probably Al segregates to the non-crystalline region in grain boundaries and forms Al—O bond.

In order to illustrate the surface morphology of the AZO films，their AFM images are shown in Fig. 2. The nanocrystalline surface of the AZO films exhibits coalescence of the grains in AZO under different sputtering powers and sputtering times. The roughness of the grown film is in the range of $2.0 \sim 6.2$nm irregularly varied with sputtering power，as represented in Fig. 2(a). The roughness of the films decreass from 6.2 to 1.0nm when the thickness of the
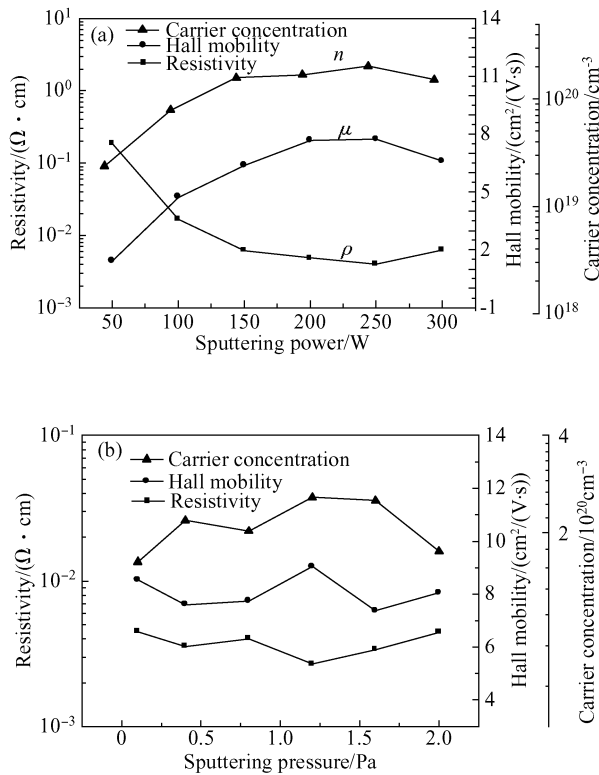
Fig.3   Resistivity，Hall mobility，and carrier concentrations as a function of sputtering power at constant Ar partial pressure of 0. 8Pa（a）and Ar pressure at constant power of 250W（b）

film increases from 180 to 360nm（time from 6 to 12min）and remains almost unchanged as 1. 0～1. 5nm when the thickness increases from 360 to 900nm（time from 12 to 30min），as shown in Fig. 2（b）. The grain size of the AZO films increases as the sputtering time increases from 12 to 30min，as Figure 2（b）shows. By the way，the roughness of the films is in the range of 5. 0～6. 2nm lightly varied with Ar partial pressure （not shown here）.

3. 2   Electrical properties

The dependence of electrical resistivity（ρ），carrier concentration（n），and mobility（μ）on various power and ambient pressure is shown in Fig. 3. The results show that all the films are degenerate doped n-type semiconductor. The plot in Fig. 3（a）indicates the resistivity of the AZO films decreases as the power increases from 50 to 250W，and the lowest resistivity is obtained at 250W. As the power further increases，the resistivity increases and reaches 6.22×10^{-3} $\Omega \cdot$ cm at 300W. As the sputtering power increases from 50 to 250W，carrier concentration and Hall mobility increase accordingly，reach the maximum at 250W，and then decrease sharply. The change of the mobility can be attributed to the change of the crystallinity. At 250W，the film exhibits the highest XRD value，i. e.，it has the best crystal quality，so Hall mob-

ility of the film is much larger than that of the films prepared at other powers. However，when the power reaches 300W，the growth rate reaches 40nm/min. And the films will be damaged by too high energy ion，limiting the crystal quality. Moreover，due to the domination of deposition acceleration effect，some adsorption atoms do not have enough time to migrate to the sites where the surface energy is the lowest and then covered by the coming atoms. The lower surface energy sites where the atoms situated means better crystal oriented，leading to lower grain boundaries scattering in the films. The plot in Fig. 3（b）indicates the lowest resistivity of $2. 68 \times 10^{-3}$ $\Omega \cdot$ cm，the highest Hall mobility of $9. 04$cm^2/（V $\cdot$ s）and the highest carrier concentration of $2. 57 \times 10^{20}$ cm^{-3} obtained at the Ar partial pressure of 1. 2Pa and power of 250W. As the Ar partial pressure further increases，the resistivity increases and reaches $4. 43 \times 10^{-3}$ $\Omega \cdot$ cm at the Ar partial pressure of 2. 0Pa. The change of resistivity under different sputtering conditions will be explained by scattering theory as follows. The resistivity of AZO film is expressed as $\rho = 1/n_e e \mu_H$，where n_e is the carrier concentration，and e and μ_H are the electron charge and Hall mobility. In such polycrystalline films，grain boundaries scattering and impurity scattering will significantly influence the mobility of the films. Minami[17] reported that the impurity scattering had dominant influence on the mobility，due to the tightness of the films deposited at high temperature. However，the films deposited at low temperature in this experiment are loose and porous，which incline to adsorb O on grain boundaries. Moreover，AES analysis shows that AZO films are not stoichiometric，i. e.，Zn/O≈0. 6. The Zn，O，and Al amount in the film was ～35at. %，～61at. %，and ～ 4at. % respectively，which implied that grain boundaries adsorb oxygen. The effect of chemisorption of oxygen on the grain boundary would capture electrons from conduction band and lead to the formation of potential barriers among the crystallites，which will influence the electric property of the AZO thin films. Therefore，grain boundaries scattering is dominant factor of the films mobility，which implied that the best AZO films with the lowest grain boundaries scattering were obtained at room temperature condition with the power of 250W and Ar partial pressure of 1. 2Pa.

Though the lowest resistivity of the AZO films that we deposited at room temperature is still higher than the films deposited at high temperature[18]，it will be improved by post rapid thermal processing （RTA）[3,19] during or after fabrication of optoelectronic devices.
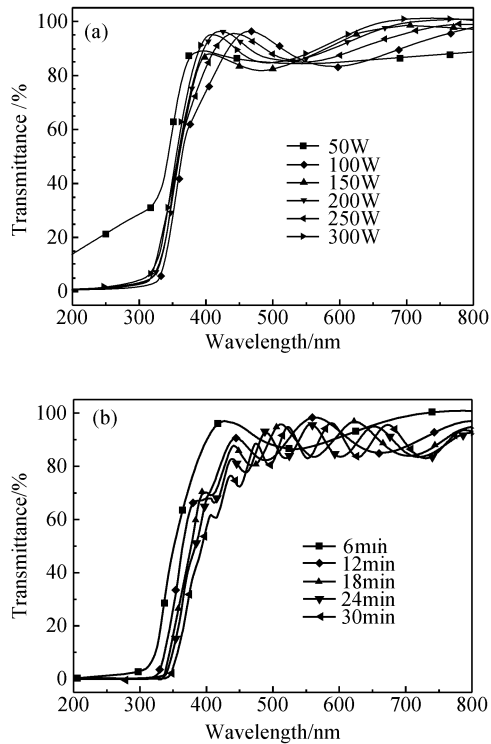
Fig. 4 Dependence of the transmission of the AZO thin films prepared at different sputtering powers of 50~300W (a) and different sputtering times of 6~30min (b)

3. 3 Optical properties

Figure 4 shows the transmission spectra in the wavelength range of 200~800nm for AZO thin films. The average optical transmittance of the AZO films in the visible range is 92. 2% ,87. 9% ,87. 0% ,86. 0% , and 84. 7% for the films of 180,360,540,720, and 900nm ,respectively. A sharp UV-off shifts to shorter wavelength with an increase in carrier concentration, known as the Burstein-Moss shift[20]. The AZO film with electron carrier concentration above $10^{20}\,\mathrm{cm}^{-3}$ degenerates and the Fermi energy penetrates into the conduction band. The optical bandgap (E_g) of the films can be obtained by plotting α^2 versus $h\nu$ (α is the absorption coefficient and $h\nu$ the photon energy) and extrapolating the linear portion of this plot to the energy axis. The E_g of the films with 180nm thickness is 3. 66eV. The obtained optical gaps of these films are much larger than those of pure ZnO ($\sim$ 3. 30eV), which can be explained by B－M effect as follows. According to the B－M effect, the energy band gap widening (ΔE_g) is related to n_e through the following equation,

$$\Delta E_g = \frac{h^2}{8m^*} \times \left(\frac{3}{\pi}\right)^{2/3} n_e^{2/3} \qquad (1)$$

where ΔE_g is the shift of doped semiconductor compared to undoped semiconductor, h is the Planck's constant, m^* is the electron effective mass in conduc-

tion band, and n_e is the electron carrier concentration. So it is considered from Eq. (1) that the increase of carrier concentration results in the broadening of the optical band gap in the heavily doped AZO films.

4 Conclusion

In summary, high-quality transparent conducting AZO films were grown on glass substrates by the RF magnetron sputtering deposition technique, showing strong c-axis orientation. The surface morphology of the films on glass substrates shows different characteristics under variable deposition condition. The films demonstrate more than 85% of the optical transparency in the visible region. The films show conductivity with a very low electrical resistivity of 2. 68×$10^{-3}\,\Omega\cdot$cm, at room temperature. By comparing the samples deposited at various RF powers, Ar pressures and sputtering times, it is indicated that the grain boundaries scattering is the dominant factor that influences the electric property of the AZO thin film.

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RF 磁控溅射制备 AZO 透明导电薄膜及其性能

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摘要： 室温下采用 RF 磁控溅射技术在石英衬底上制备了多晶 ZnO：Al（AZO）透明导电薄膜，通过 XRD，AFM，AES，Hall 效应及透射光谱等测试研究了 RF 溅射功率、氩气压强对薄膜的结构、电学和光学性能的影响. 分析表明：在最优条件下（溅射功率为 250W，氩气压强为 1.2Pa 时），180nm AZO 薄膜的电阻率为 $2.68×10^{-3}$ Ω·cm，可见光区平均透射率为 90%，适合作为发光二极管和太阳能电池的透明电极. 所制备的 AZO 薄膜具有 c 轴择优取向，晶粒间界中的 O 原子吸附是限制薄膜电学性能的主要因素.

关键词： RF 磁控溅射；透明导电薄膜；AZO 薄膜
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