Influence of the sputtering pressure on the properties of transparent conducting zirconium-doped zinc oxide films prepared by RF magnetron sputtering

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Abstract: Transparent conducting zirconium-doped zinc oxide films with high transparency and relatively low resistivity have been successfully prepared on water-cooled glass substrate by radio frequency magnetron sputtering at room temperature. The Ar sputtering pressure was varied from 0.5 to 3 Pa. The crystallinity increases and the electrical resistivity decreases when the sputtering pressure increases from 0.5 to 2.5 Pa. The cystallinity decreases and the electrical resistivity increases when the sputtering pressure increases from 2.5 to 3 Pa. When the sputtering pressure is 2.5 Pa, it is obtained that the lowest resistivity is 2.03×10^{-3} Ω·cm with a very high transmittance of above 94%. The deposited films are polycrystalline with a hexagonal structure and a preferred orientation perpendicular to the substrate.

Key words: zirconium-doped zinc oxide films; transparent conducting films; magnetron sputtering; sputtering pressure

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1. Introduction

Transparent conducting oxides (TCO) are widely used in microelectronic devices such as liquid crystal displays, organic light-emitting diodes, and thin film solar cells[1−3]. Presently, tin-doped indium oxide (ITO) film is the most widely used TCO film due to its high transparency, low resistivity and high work function. In applications involving transparent heaters and chemical sensors, it is required that the films be chemically stable as they cycle through high temperatures. However, ITO films are not stable and show degradation at temperatures above 700 K[4]. ZrO_2–ZnO films are stable and exhibit no evidence of micro-cracking after multiple cycles over a wide range of temperatures[5]. Zirconium-doped zinc oxide (ZZO) film is a promising substitute of ITO to work at high temperatures (> 700 K) stably. Moreover, ZZO films are nontoxic, inexpensive and abundant compared with ITO.

Studies on ZZO are rarely reported. The highest transmittance of ZZO film prepared by pulsed-laser deposition was only 88%[6], the lowest resistivity of ZZO film prepared by sol-gel method was 7.2×10^{-2} Ω·cm[7], and the lowest resistivity of ZZO films prepared by magnetron sputtering at room temperature was 2.07×10^{-3} Ω·cm with a transmittance of about 90%[8]. In this paper, ZZO films with good adhesion have been successfully prepared on water-cooled glass substrate by RF magnetron sputtering. The structural, morphological, electrical and optical properties of the films were analyzed in detail with the variation of sputtering pressure. The lowest resistivity of ZZO film is 2.03×10^{-3} Ω·cm with a very high transmittance of above 94%.

2. Experiment

The ZZO films were deposited on water-cooled glass substrates in a GJP500C2 model RF magnetron sputtering system with a radio frequency of 13.56 MHz and a basic pressure of 3.4×10^{-4} Pa. During the process of deposition, the sputtering RF power was maintained at 150 W and the sputtering time was controlled at 40 min for all the films. A sintered ceramic with a mixture of ZnO (99.99% purity) and ZrO_2 (99.99% purity) was employed as source material. The content of ZrO_2 added to the ZnO target was 5 wt.%. The distance between the substrate and the target was about 60 mm. During the sputtering, the substrates were water-cooled and almost kept at room temperature. In order to investigate the effect of sputtering pressure on the properties of ZZO films, the sputtering pressure was varied from 0.5 to 3 Pa. Prior to the deposition, the glass substrates were ultrasonically cleaned in acetone for 15 min, marinated in alcohol for 10 min and washed by purified water.

The structural properties of the films were analyzed with a D8 ADVANCE XRD using CuKα_1 radiation (λ = 0.15406 nm) and the surface morphologies were analyzed by using a Sirion 200 SEM. The optical transmittance measurements were performed with a TU-1901 UV-VIS spectrophotometer. The sheet resistance R was measured at room temperature with a SDY-4 four-point probe measurement. The thickness (l) of the films was measured using a SGC-10 thin film thickness tester. The resistivity of ZZO films was evaluated using the formula $\rho = Rl$.

3. Results and discussion

3.1. Growth rate of ZZO films

Figure 1 shows the dependence of the growth rate on the sputtering pressure. It is observed that the growth rate decreases as the sputtering pressure increases from 0.5 to 2 Pa and 2.5 to 3 Pa, whereas the growth rate increases as the

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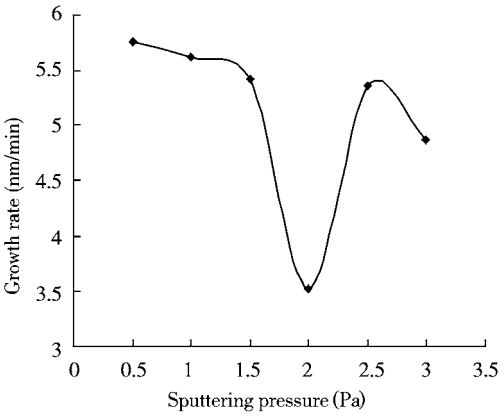

Fig.1. Dependence of growth rate on the sputtering pressure.

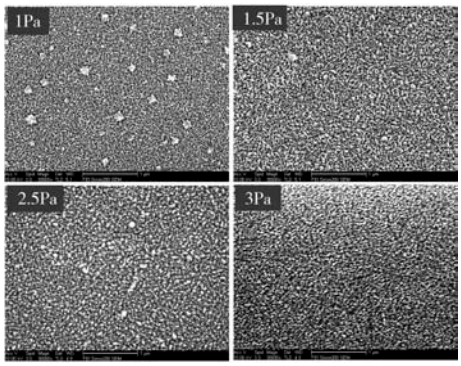

Fig.2. Surface morphologies of the ZZO films at various Ar sputtering pressure.

sputtering pressure increases from 2 to 2.5 Pa. For higher sputtering pressure, the mean free path (4 mm at 2.0 Pa) decreases and the sputtered species including atoms, molecules and ions undergo more collisions resulting in a thermalization of the film-forming particles. Therefore, the surface mobility of these species decreases and hence the growth rate also decreases[9]. On the other hand, for higher sputtering pressure, the density of molecule increases, the number of the sputtered species landing onto the surface in a second increases leading to the increase of the growth rate. In our experiments, when the sputtering pressure increases from 0.5 to 2 Pa and 2.5 to 3 Pa, the former effect should be dominant and then the growth rate decreases. When the sputtering pressure increases from 2 to 2.5 Pa, the latter effect is much more important and thus the growth rate increases.

3.2. Structural characterization of ZZO films

Figure 2 shows the surface morphologies of ZZO films at various Ar sputtering pressure. From the micrographs, an obvious increase of crystallite size is observed when the sputtering pressure increases from 1 to 2.5 Pa, and the surface roughness is also increased simultaneously. As the sputtering pressure increases from 2.5 to 3 Pa, the crystallite size decreases obviously. The decrease of the sputtering pressure will lead to three effects: (1) For lower sputtering pressure, the mean free path increases, the sputtered species undergo less collisions between the substrate and the target and hence the kinetic energy of the sputtered species increases, which causes an increase of the particles' mobility in the surface of the film. The

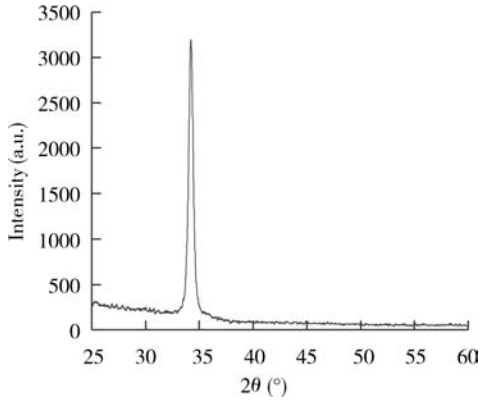

Fig.3. XRD spectrum of ZZO film deposited on water-cooled glass substrate at 2.5 Pa.

particles (including molecules, atoms, ions and their clusters) under a larger driving force can migrate to more suitable lattice sites and adjust their own bond direction and length to obtain optimum bonding to the adjacent ones, which are helpful for nucleation and growth, and consequently the crystallinity is increased and the crystallite size is improved[10]. (2) The surface damage caused by bombardment of the sputtered particles increases[11]. It is proposed that the kinetic energy of particles increases with decreasing the sputtering pressure, so lower pressure can enhance the lattice damage by the high-energy particles, which deteriorates the crystallinity[12]. (3) The stability of the sputtering system deteriorates with the decrease of the pressure[13], which is not in favor of the cyrstallinity. As the sputtering pressure increases from 2.5 to 3 Pa, the first effect dominates and the crystallinity is deteriorated. While the sputtering pressure increases from 1 to 2.5 Pa, the second and the third effect mentioned above is in the ascendant leading to the increase of the cystallinity.

Figure 3 shows the X-ray diffraction spectrum of ZZO film deposited on water-cooled glass substrate at room temperature at 2.5 Pa. The θ–2θ scan data of the ZZO film only exhibits a strong peak at $2\theta = 34.20^\circ$, which is very close to the preferred orientation of the standard ZnO crystal (34.45°) and corresponding to the (002) peak. This indicates that the ZZO film is polycrystalline with a hexagonal structure and a preferred orientation perpendicular to the substrate. No ZrO_2 phase was detected from XRD curve. This may be due to zirconium replacing zinc substitutionally in the hexagonal lattice or zirconium segregating to the non-crystalline region in grain boundary. The full-width at half-maximum (FWHM) of the (002) diffraction peak is calculated as 0.54°, and then the crystallite size is calculated as 17.6 nm according to the Scherre formula $D = 0.89\lambda/(B\cos\theta)$. Thus we can conclude that the ZZO film deposited on glass substrate is nanostructural crystal.

3.3. Electrical properties of ZZO films

The dependence of the electrical resistivity and sheet resistance of the ZZO films on the sputtering pressure is depicted in Fig.4. With the increase of sputtering pressure, both the electrical resistivity and sheet resistance first decrease and

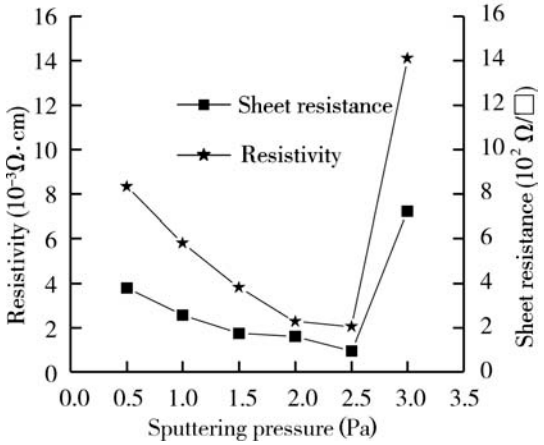

Fig.4. Dependence of the electrical resistivity and sheet resistance on the Ar sputtering pressure for the ZZO films deposited on water-cooled glass substrate.

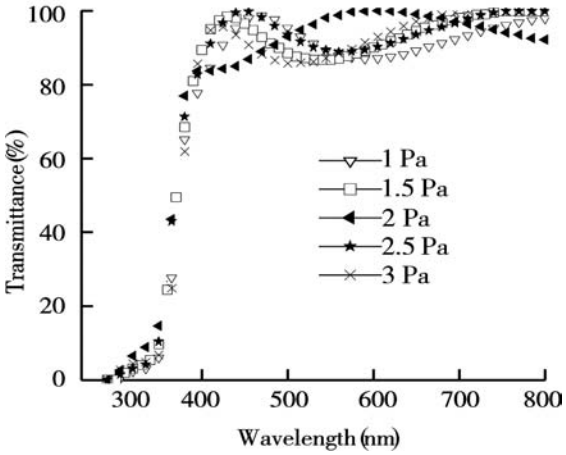

Fig.5. Transmittance as a function of wavelength for ZZO films deposited at different pressures.

then increase sharply. The increase of conductivity can be attributed to the improvement of crystallinity with the increase of the crystallite size. A larger crystallite size results in a lower density of grain boundaries, which behave as traps for free carriers and barriers for carrier transport. Hence, an increase in the crystallite size can cause a decrease in grain-boundary scattering and an increase in carrier lifetime and carrier concentration[14], and consequently leads to an increase in both the carrier concentration and Hall mobility and hence the electrical resistivity and sheet resistance decrease. With the improvement of crystallinity, the concentration of electrically active donor sites is improved, which can also increase the carrier concentration[15]. A reduction of the ionized impurity scattering may be another reason of the higher Hall mobility[16]. As mentioned above, when the pressure increases from 0.5 to 2.5 Pa, the crystallite size increases leading to both the electrical resistivity and sheet resistance decrease. While the deposition increases from 2.5 to 3 Pa, the crystallite size decreases resulting in the electrical resistivity and sheet resistance increase. When the pressure is 2.5 Pa, it is obtained that the lowest resistivity is 2.03×10^{-3} Ω·cm with a sheet resistance of 94.8 Ω/□.

3.4. Optical properties of ZZO films

Figure 5 shows the optical transmittance in the UV-VIS region of ZZO films deposited at various sputtering pressures. When the sputtering pressure is 1, 1.5, 2.0, 2.5, and 3 Pa, the average transmittance (in the wavelength range of 500–800 nm) of ZZO films is 92%, 94%, 97%, 94%, and 95%, respectively. The absorption coefficient of ZZO films was evaluated using the formula $\alpha = (1/l)\ln(1/T)$, where l is the film thickness and T is the transmittance of ZZO films.The optical band gap (E_g) was determined by extrapolation of the straight region of the plot of square of the absorption coefficient (α^2) versus of photon energy ($h\nu$)[6]. The optical band gap values for ZZO films decrease from 3.59 to 3.48 eV when the sputtering pressure increases from 0.5 to 3 Pa. This means that the sputtering pressure affects the band gap of ZZO films, which agrees with what Shui *et al.* concluded[17].

4. Conclusion

ZZO films with high transparency and relatively low resistivity have been successfully prepared on water-cooled glass substrate by radio frequency magnetron sputtering at room temperature. The experimental results indicate that the Ar sputtering pressure plays an important role on the crystallite size and the electrical properties of ZZO films. When the sputtering pressure increases from 0.5 to 2.5 Pa, the crystallite size increases and the electrical resistivity decreases. When the sputtering pressure increases from 2.5 to 3 Pa, the crystallite size decreases and the electrical resistivity increases. When the sputtering pressure is 2.5 Pa, it is obtained that the lowest resistivity is 2.03×10^{-3} Ω·cm with a very high transmittance of above 94%. The deposited films are polycrystalline with a hexagonal structure and a preferred orientation perpendicular to the substrate.

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