Preparation and characterization of transparent conducting ZnO:W films by DC magnetron sputtering*

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Abstract: Tungsten-doped zinc oxide (ZnO:W) films with low resistivity and high transmittance were successfully deposited on glass substrates by direct current magnetron sputtering at low temperature. The deposition pressure is varied from 12 to 21 Pa. The X-ray diffraction results show that all of the deposited films are polycrystalline and have a hexagonal structure with a preferred c-axis orientation. The crystallinity, morphologies and resistivity of ZnO:W films greatly depend on deposition pressure while the optical properties including optical transmittance, optical band gap as well as refractive index are not sensitive to deposition pressure. The deposited films with an electrical resistivity as low as 1.5×10^{-4} Ω·cm，sheet resistance of 6.8 Ω/□ and an average transmittance of 91.3% in the visible range were obtained at a deposition pressure of 21 Pa and sputtering power of 130 W.

Key words: tungsten-doped zinc oxide; transparent conducting films; magnetron sputtering; deposition pressure
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1. Introduction

Recently transparent conducting oxides (TCO) have been paid much more attention because they are widely used in optoelectronic devices, such as thin film solar cells and liquid crystal display[1, 2]. Tin-doped indium oxide (ITO) is the most widely used TCO film due to its excellent electrical and optical properties. However, high cost as well as toxicity of ITO films greatly limits its practical applications in the above fields. In order to satisfy the expanding market demands, new type TCO films must be developed[3]. Among new TCO films, zinc oxide film is the most promising alternative to ITO and has been actively studied on account of its low cost, innocuity, low deposition temperature and chemical stability under hydrogen plasma processes that are commonly used for the production of solar cells[4, 5]. Up to now, developing new TCO films still remain quite attractive and interesting. However, to the best of our knowledge, transparent conducting ZnO:W thin films have rarely been reported. Doping tungsten into zinc oxide is quite attractive due to the high valence difference between W^{+6} and Zn^{+2}. On the other hand, DC magnetron sputtering is outstanding for the preparation of transparent conducting thin films because of its advantages, such as high growth rate, low deposition temperature, low cost and large-area films. Therefore, it is necessary to study ZnO:W films deposited by DC magnetron sputtering.

We have successfully prepared transparent conducting ZnO:W films using DC magnetron sputtering and reported the properties with variation in film thickness[6]. In this work, highly conducting and transparent ZnO:W thin films are deposited on glass substrate by DC magnetron sputtering, and the optical, structural and electrical properties of ZnO:W thin films are investigated systematically with variation in deposition pressure.

2. Experimental details

ZnO:W films were fabricated on unheated glass substrates by DC magnetron sputtering. A sintered ceramic target (75 mm diameter, 3 mm thickness) with a mixture of ZnO (99.99% purity) and WO_3 (99.99% purity) was employed as source material and the content of WO_3 was 7 wt.%. The basic pressure of the sputtering system was 6.8×10^{-4} Pa. The glass substrates were ultrasonically cleaned in acetone for 10 min, immersed in alcohol for 30 min and washed by purified water. During the process of deposition, the deposition time and target-to-substrate distance were controlled at 30 min and 6 cm, respectively. The deposition pressure of Ar (99.99%) was varied from 12 to 21 Pa while DC sputtering power was maintained at 100 and 130 W.

The optical transmittance of the films was measured by UV–vis spectrophotometers. The refractive index and thickness were measured with a SGC-10 thin film thickness tester. The surface morphologies were analyzed using a Sirion 200 SEM apparatus. The crystal quality of the films was analyzed with a D8 ADVANCE XRD system using CuKα1 radiation (λ = 0.15406 nm). The sheet resistance was measured with a four-point probe measurement system at room temperature. The electrical resistivity was determined by taking the product of sheet resistance and film thickness.

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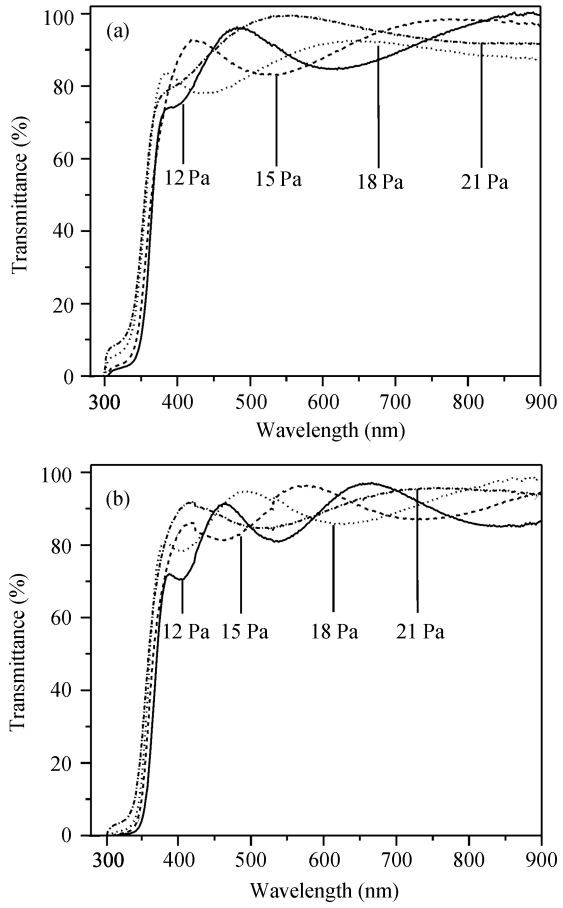

Fig. 1. Effect of deposition pressure on transmittance spectra for ZnO:W films. (a) 100 W. (b) 130 W.

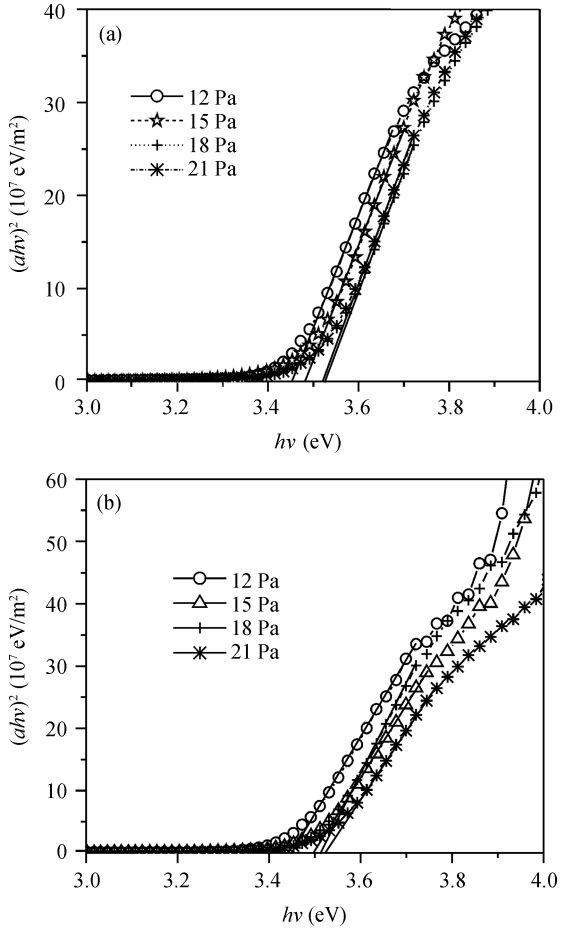

Fig. 2. Plots of $(\alpha hv)^2$ versus hv for ZnO:W films deposited at different deposition pressure. (a) 100 W. (b) 130 W.

3. Results and discussion

3.1. Optical properties of ZnO:W films

Figure 1 shows the optical transmittance in the UV-vis region of ZnO:W films deposited at different deposition pressures. It is found that the transmittance does not change much with the increase in deposition pressure, and the average transmittance for all of the deposited films is approximately 90%. The average transmittance is calculated by taking the average value of the transmittance in the range 400–800 nm of all of the deposited films.

The optical band gap was determined by extrapolation of the straight region of the plot of $(\alpha hv)^2$ versus of hv[7]. As shown in Fig. 2, the optical band gap value continuously increases from 3.45 to 3.52 eV as the pressure increases from 12 to 15 Pa. This value is larger than that of pure ZnO film due to the famous Burstein–Moss (BM) effect. When W atoms are deeply doped into ZnO films, the lower levels in the conduction band are occupied by electrons, resulting in an increase in Fermi level and then the optical band gap widens. The optical band gap of the film deposited at higher pressure is larger than that deposited at lower pressure, suggesting that the higher pressure is more helpful for the effective substitution of Zn^{2+} ions by W^{6+} ions releasing excess electrons into the conduction band. This is in accordance with the change of the electrical conductivity with the variation in deposition pressure discussed later.

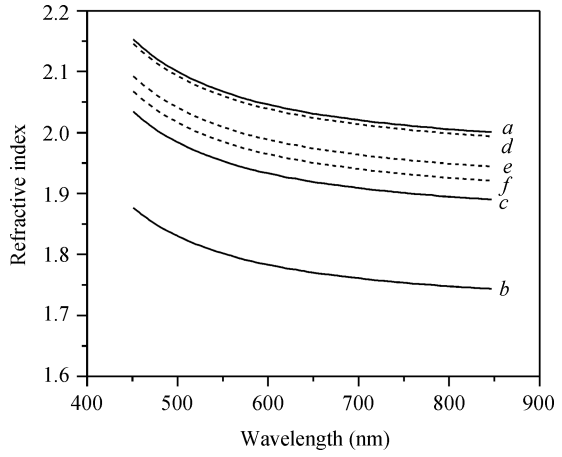

Fig. 3. Refractive index of ZnO:W films as a function of wavelength. (*a*) 100 W and 12 Pa. (*b*) 100 W and 15 Pa. (*c*) 100 W and 21 Pa. (*d*) 130 W and 12 Pa. (*e*) 130 W and 15 Pa. (*f*) 130 W and 21 Pa.

Figure 3 shows the refractive index of ZnO:W films deposited at different pressure as a function of wavelength. As shown in Fig. 3, the refractive index of the films decreases with increase in wavelength. For the films deposited at 100 W, the average refractive index in the wavelength of 450–850 nm decreases from 2.04 to 1.78 as the pressure increases from 12 to

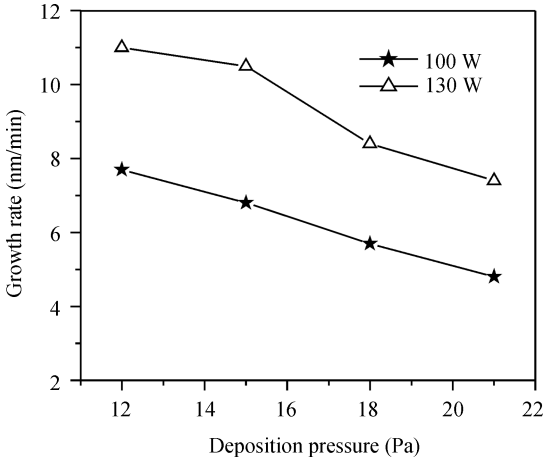

Fig. 4. Growth rate of ZnO:W films as a function of deposition pressure.

15 Pa, and then increases to 1.93 at a pressure of 21 Pa. However, for the films deposited at 130 W, the average refractive index decreases continuously from 2.04 to 1.96 as the pressure increases from 12 to 21 Pa.

3.2. Growth rate of ZnO:W films

Figure 4 shows the variation in growth rate with deposition pressure. It is found that the growth rate obviously increases as the deposition pressure decreases from 21 to 12 Pa. For lower pressure, the sputtered species undergo fewer collisions before arriving at the substrate surface due to the increase in mean free path, and hence the kinetic energy of these species increases. This is helpful for nucleation and growth, resulting in an increase in growth rate. We can also find that the growth rate of ZnO:W films deposited at 130 W is higher than that deposited at 100 W under the same pressure due to the higher self-polarization potential at lower pressure[8].

3.3. Structural characterization of ZnO:W films

Figure 5 shows the SEM images of the ZnO:W films deposited at different deposition pressures. We find that deposition pressure plays an important role in film surface structure. When the deposition pressure is 12 Pa, the grains are very small, and they interact with each other and agglomerate, so every particle consists of many small grains. When the deposition pressure increases to 15 Pa, the film structure is composed of many columnar structured grains. However, when the pressure is 21 Pa, the film structure consists of many flat and irregular grains. One can find that the grain size increases rapidly as the pressure increases. For lower deposition pressures, the sputtered species have higher kinetic energy and higher surface mobility, which increases the probability of forming nuclei but limits the nuclei growth, resulting in small grain structure.

Figure 6 shows the XRD patterns of ZnO:W films deposited under different deposition pressure. All of the deposited films show (002) and (101) peaks, but the intensity of the (101) peak is much weaker than that of the (002) peak. This indicates that all of the films show a preferred orientation along the *c*-axis perpendicular to the substrate. The intensity increases markedly with an increase in deposition pressure

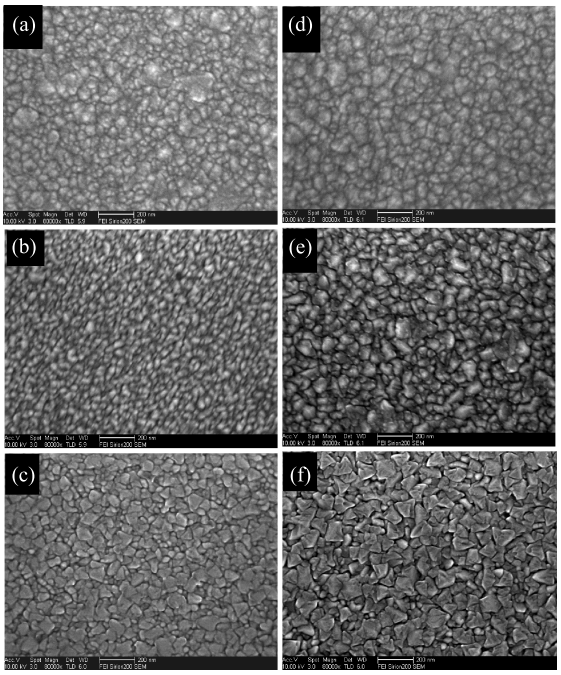

Fig. 5. SEM images of ZnO:W films. (a)100W and 12 Pa. (b) 100 W and 15 Pa. (c) 100 W and 21 Pa. (d) 130 W and 12 Pa. (e) 130 W and 15 Pa. (f) 130 W and 21 Pa.

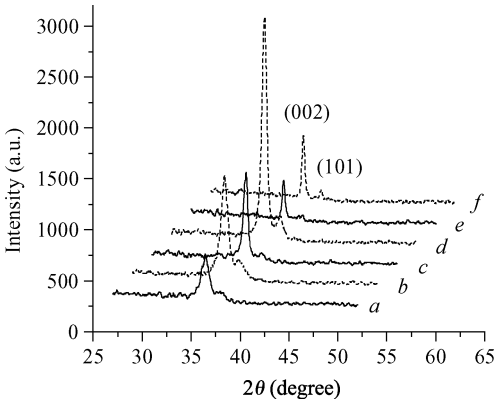

Fig. 6. XRD patterns of ZnO:W films. (*a*) 100 W and 12 Pa. (*b*) 130 W and 12 Pa. (*c*) 100 W and 15 Pa. (*d*) 130 W and 15 Pa. (*e*) 100 W and 21 Pa. (*f*) 130 W and 21 Pa.

up to 15 Pa and, above this pressure, the intensity decreases obviously with further increase in deposition pressure. However, as the deposition pressure increases, the position of the (002) peak does not change much. On the other hand, as the deposition pressure increases from 12 to 21 Pa, the full-width at half-maximum value decreases continuously while the crystallite size increases from 8 to 25 nm, indicating an improvement in the crystal quality, which is consistent with the SEM results mentioned above. We can also find that the intensity of the (002) peak for ZnO:W films deposited at 130 W is much larger than that deposited at 100 W under the same pressure.

3.4. Electrical properties of ZnO:W films

Figure 7 shows the dependence of the electrical properties of the ZnO:W films on the deposition pressure. We find that

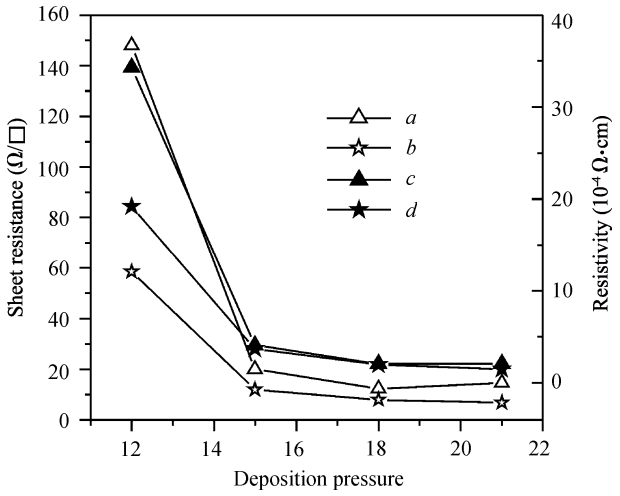

Fig. 7. Dependence of sheet resistance and resistivity for ZnO:W films on deposition pressure. (*a*) 100 W, sheet resistance. (*b*) 130 W, sheet resistance. (*c*) 100 W, resistivity. (*d*) 130 W, resistivity.

the sheet resistance decreases rapidly with an increase in the pressure up to 15 Pa and then decreases slowly with further increase in the pressure. The tendency of the change in electrical resistivity is in agreement with the sheet resistance. Moreover, under the same pressure, the electrical properties of the films deposited at 130 W are always better than those at 100 W. The films with resistivity as low as 1.5×10^{-4} Ω·cm and a small sheet resistance of 6.8 Ω/□ are obtained at a deposition pressure of 21 Pa and sputtering power of 130 W. In previous reports, the lowest resistivity of ZnO:Al[9] and ZnO:Ga[10] films were 4.97×10^{-4} Ω·cm and 2.6×10^{-4} Ω·cm, respectively. The increase in electrical conductivity can be attributed to the improvement in crystal quality with an increase in the crystallite size due to the increase in carrier lifetime as well as carrier concentration[11−13]. As mentioned above, when the pressure increases, the crystallite size also increases with an associated decrease in the resistivity.

4. Conclusions

Highly conducting and transparent thin films of ZnO:W were successfully prepared on unheated glass substrates by DC magnetron sputtering. All of the deposited films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. The crystallinity, resistivity and morphologies of ZnO:W films greatly depend on deposition pressure while the optical transmittance, optical band gap and refractive index are not sensitive to deposition pressure. The deposited films with an electrical resistivity as low as 1.5×10^{-4} Ω· cm, a sheet resistance of 6.8 Ω/□, an average transmittance of 91.3% and a refractive index of 1.96 in the visible range were obtained at a deposition pressure of 21 Pa and a sputtering power of 130 W.

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