

# Thickness dependence of the properties of transparent conducting ZnO:Zr films deposited on flexible substrates by RF magnetron sputtering

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**Abstract:** Transparent conducting zirconium-doped zinc oxide (ZnO:Zr) thin films with high transparency, low resistivity and good adhesion were successfully prepared on water-cooled flexible substrates (polyethylene glycol terephthalate, PET) by RF magnetron sputtering. The structural, electrical and optical properties of the films were studied for different thicknesses in detail. X-ray diffraction (XRD) and scanning electron microscopy (SEM) revealed that all the deposited films are polycrystalline with a hexagonal structure and a preferred orientation perpendicular to the substrate. The lowest resistivity achieved is  $1.55 \times 10^{-3} \Omega\cdot\text{cm}$  for a thickness of 189 nm with a Hall mobility of  $17.6 \text{ cm}^2/(\text{V}\cdot\text{s})$  and a carrier concentration of  $2.15 \times 10^{20} \text{ cm}^{-3}$ . All the films present a high transmittance of above 90% in the wavelength range of the visible spectrum.

**Key words:** zirconium-doped zinc oxide thin films; flexible substrates; magnetron sputtering; transparent conducting films

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## 1. Introduction

Transparent conducting thin films deposited on flexible substrates have many merits such as lightweight, small volume and making the devices folded and easily carried. They are widely used in flexible electro-optical devices, flexible liquid crystal displays, plastic thin film solar cells, transparent electromagnetic shielding materials and unbreakable heat reflecting mirrors<sup>[1]</sup>. In recent years, Sn-doped  $\text{In}_2\text{O}_3$  (ITO) films on flexible substrates have been extensively studied<sup>[2-4]</sup>. But in our knowledge, no report was published for ZnO:Zr films prepared on flexible substrates up to now. Moreover, ZnO:Zr films are nontoxic, inexpensive and abundant compared with ITO<sup>[5]</sup>. The organic material PET has good transmittance, high melting point (about 200 °C), low cost and low chemical reactivity. Thus, it is necessary to study ZnO:Zr films deposited on PET substrate. In this paper, the preparation of transparent conducting ZnO:Zr films deposited on flexible PET substrate using RF sputtering magnetron method is reported. The structural, morphological, electrical and optical properties of the films are analyzed in detail with the variation of the film thickness.

## 2. Experiment

The ZnO:Zr films with different thicknesses were deposited on flexible PET substrates in a GJP500C2 model RF magnetron sputtering system with a basic pressure of  $3.4 \times 10^{-4}$  Pa. A sintered ceramic with a mixture of ZnO (99.99% purity) and  $\text{ZrO}_2$  (99.99% purity) was employed as source material. The content of  $\text{ZrO}_2$  added to the ZnO target was 5 wt.%. The distance between the substrate and the target was about 50 mm. During the deposition, the pressure of Ar was

controlled at 1.5 Pa, and the sputtering RF power was maintained at 100 W for all the films. During the sputtering, the substrates were water-cooled and kept at room temperature. In order to investigate the effect of the thickness on the properties of ZnO:Zr films, the deposition time was varied from 20 to 60 min. Prior to the deposition, the PET 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  $\text{CuK}\alpha_1$  radiation ( $\lambda = 0.15406$  nm) and the surface morphologies were analyzed by using a Sirion 200 SEM. The thickness of the films was measured using a  $\alpha$  step 250R surface-profile-measure system. The electrical properties (resistivity, Hall mobility and carrier concentration) were measured by four point probe method and Hall effect measurements using the van der Pauw technique at a constant magnetic field of 0.5 T. The optical transmittance measurements were performed with a TU-1901 UV-VIS spectrophotometer.

## 3. Results and discussion

### 3.1. Film thickness

Figure 1 shows the variation of the film thickness with deposition time. It is found that the thickness increases nearly linearly from 104 to 245 nm when the deposition time increases from 20 to 60 min<sup>[5]</sup>.

### 3.2. Structural characterization

Figure 2 shows the X-ray diffraction patterns of the ZnO:Zr films with different thicknesses deposited on water-cooled PET substrates. It revealed that all the deposited films

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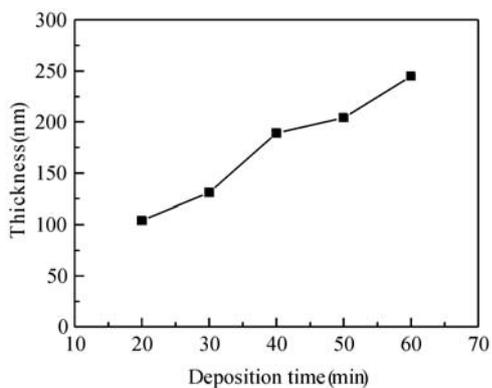


Fig. 1. Dependence of the film thickness on the deposition time for ZnO:Zr films deposited on water-cooled PET substrates.

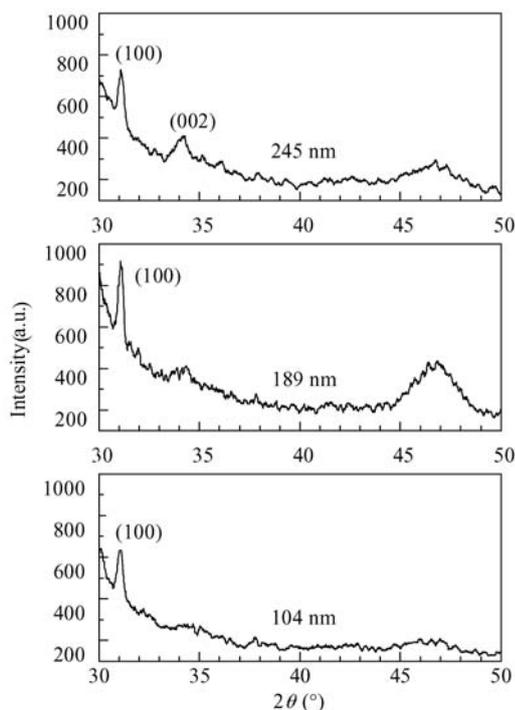


Fig. 2. X-ray diffraction patterns of ZnO:Zr films deposited on water-cooled PET substrates with different thicknesses.

are polycrystalline with the hexagonal structure and a preferred orientation perpendicular to the substrate. All the films show a strong (100) peak at  $2\theta \approx 31.26^\circ$ , which is very close to that of the standard ZnO crystal ( $31.45^\circ$ ). When the thickness is 245 nm, the ZnO (002) peak appears, but its intensity is much weaker than the (100) peak. A previous study performed by Paul *et al.*<sup>[6]</sup> showed that the preferred orientation for ZnO:Zr films was dependent on the experimental conditions, but the reason is ambiguous up to now. No ZrO<sub>2</sub> phase was detected from XRD patterns. This may be due to zirconium replacing zinc substitutionally in the hexagonal lattice or zirconium segregating to the non-crystalline region in grain boundary. As exhibited in Fig. 2, when the thickness increases, the location of the detected diffraction peaks does not change significantly, but the intensity of the peaks becomes more intense and sharper, and then becomes weaker and blunter. This is due to the changes of crystallite size with thickness increase.

The crystallite size can be evaluated using the Scherre

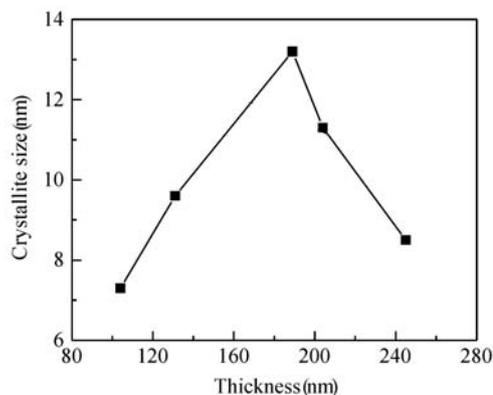


Fig. 3. Crystallite size of the ZnO:Zr films deposited on water-cooled PET substrates as a function of thickness.

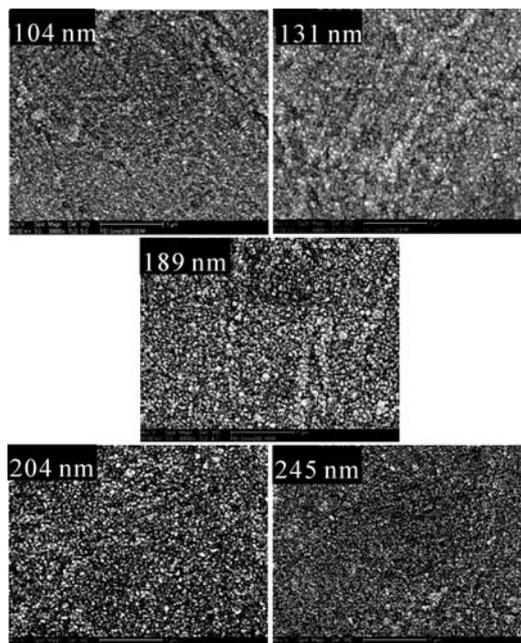


Fig. 4. SEM images of the ZnO:Zr films deposited on PET substrates with different thicknesses.

formula  $D = 0.89\lambda/B\cos\theta$ , as shown in Fig. 3. As the thickness increases from 104 to 189 nm, the crystallite size increases from 7.3 to 13.2 nm and then decreases to 8.5 nm as the thickness increases further to 245 nm.

The film thickness dependence of the crystallite sizes for ZnO:Zr films deposited on water-cooled PET substrate were also revealed by their SEM images. Figure 4 shows the SEM images of the ZnO:Zr films with different thicknesses. From these micrographs, an obvious increase of grain size is observed when the film thickness increases from 104 to 189 nm, and the surface roughness is also increased simultaneously. As the thickness increases from 189 to 245 nm, the grain size decreases obviously. The results are consistent with the XRD observation.

### 3.3. Electrical properties

Figure 5 shows the dependence of the electrical resistivity, Hall mobility and carrier concentration on the film thickness of ZnO:Zr films deposited on water-cooled PET substrates. From the XRD results discussed above, it is concluded

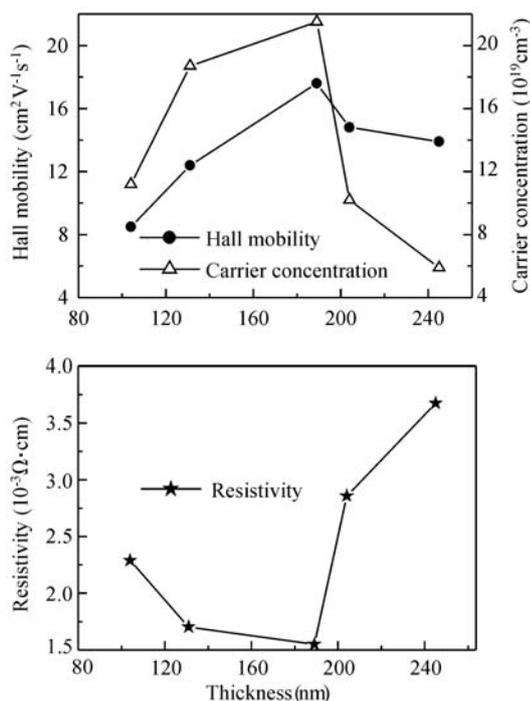


Fig. 5. Dependence of the electrical resistivity, Hall mobility and carrier concentration on the film thickness for ZnO:Zr films deposited on water-cooled PET substrates.

that the  $Zr^{4+}$  is substituted for  $Zn^{2+}$  as donor in the hexagonal structure. Thus, two free electrons are produced for each  $Zn^{2+}$  replaced by  $Zr^{4+}$ , which contribute to the electric conduction of the films as free carriers. A similar explanation has been presented for Zr-doped ZnO films deposited on glass substrates<sup>[7]</sup>. The mobility of the film is mainly determined by grain-boundary scattering and ionized-impurity scattering in extrinsic doped semiconductors. The resultant mobility  $\mu$  can be obtained from  $1/\mu = 1/\mu_{GB} + 1/\mu_{IS}$ , where  $\mu_{GB}$  is the mobility due to grain-boundary scattering and  $\mu_{IS}$  is the mobility due to ionized-impurity scattering. As mentioned above, the crystallite size changes obviously with the film thickness, so the variation of the mobility of ZnO:Zr films can be attributed to the grain-boundary scattering.

As the thickness increases from 104 to 189 nm, the resistivity decreases from  $2.29 \times 10^{-3}$  to  $1.55 \times 10^{-3}$   $\Omega\cdot\text{cm}$  due to the increase of both Hall mobility and carrier concentration. However, the resistivity increases sharply from  $1.55 \times 10^{-3}$  to  $3.68 \times 10^{-3}$   $\Omega\cdot\text{cm}$  because of the decrease of both Hall mobility and carrier concentration as the thickness increases from 189 to 245 nm. Similar variation of the resistivity with the thickness was reported in Al-doped zinc oxide (AZO) films<sup>[8]</sup> and ZnO:Zr films deposited on glass substrates<sup>[5]</sup>. When the thickness is 189 nm, it is obtained that the lowest resistivity is  $1.55 \times 10^{-3}$   $\Omega\cdot\text{cm}$  with a Hall mobility of  $17.6 \text{ cm}^2/(\text{V}\cdot\text{s})$  and a carrier concentration of  $2.15 \times 10^{20} \text{ cm}^{-3}$ . In previous studies, the lowest resistivity of ZnO:Zr films deposited on glass substrates by sol-gel method<sup>[6]</sup> and magnetron sputtering<sup>[9]</sup> was  $7.2 \times 10^{-2}$  and  $2.07 \times 10^{-3}$   $\Omega\cdot\text{cm}$ , respectively. The increase of conductivity can be attributed to the improvement of crystallinity with the increase of the crystallite size, which is

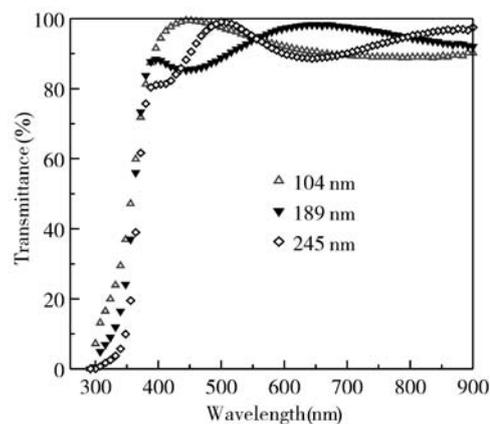


Fig. 6. Optical transmittance as a function of the wavelength for ZnO:Zr films with different thicknesses.

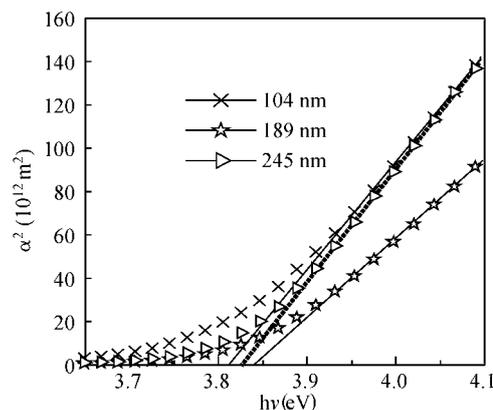


Fig. 7. Square of the absorption coefficient as a function of photon energy.

proved by the results of both XRD and SEM studies. When the thickness increases from 104 to 189 nm, the crystallite size increases and the crystallinity is improved. When the thickness increases from 189 to 245 nm, the crystallite size decreases and the crystallinity is deteriorated. 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 of carrier lifetime and carrier concentration<sup>[7,8]</sup>, and consequently leads to an increase of conductivity because of the increase of both carrier concentration and Hall mobility. With the improvement of crystallinity, the concentration of electrically active donor sites is improved, which can also increase the carrier concentration<sup>[10]</sup>. A reduction of the ionized impurity scattering in the thicker films may be another reason of the higher Hall mobility<sup>[11]</sup>.

### 3.4. Optical properties

Figure 6 shows the optical transmittance in the UV-VIS region of ZnO:Zr films with different thicknesses. The transmittance of PET substrates is about 98% in the visible spectrum. The average transmittance in the wavelength range of 390–760 nm is over 90% for all the films. The optical band gap ( $E_g$ ) was determined by extrapolation of the straight region of the plot of square of the absorption coefficient ( $\alpha^2$ ) versus of photon energy ( $h\nu$ )<sup>[12]</sup>. As shown in Fig. 7, the optical

band gap value is about 3.83 eV for all the films deposited on PET substrates with different thicknesses. When  $Zr^{+4}$  ions are deeply doped into ZnO films, the lower levels in conduct band are occupied by electrons, leading to the increase of Fermi level and then the optical band gap widens, which is known as the Burstein–Moss effect.

#### 4. Conclusions

ZnO:Zr thin films with high transparency, low resistivity and good adhesion were firstly successfully prepared on water-cooled flexible substrates PET by RF magnetron sputtering. The structural, electrical and optical properties of the films were studied for different thickness in detail. XRD and SEM revealed that all the deposited films are polycrystalline with a hexagonal structure and a preferred orientation perpendicular to the substrate. The lowest resistivity achieved is  $1.55 \times 10^{-3} \Omega\cdot\text{cm}$  for a thickness of 189 nm with a Hall mobility of  $17.6 \text{ cm}^2/(\text{V}\cdot\text{s})$  and a carrier concentration of  $2.15 \times 10^{20} \text{ cm}^{-3}$ . All the films present a high transmittance of above 90% in the wavelength range of the visible spectrum. The results may be useful for inaugurating the potential applications of ZnO:Zr films in flexible devices.

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