Preparation and character of ZnO:Al transparent conductive films deposited on polymer substrates by RF magnetron sputtering

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Aluminium doped ZnO (ZnO:Al) films were deposited on polymer substrates by RF magnetron sputtering. The influences of Al-doping concentration and deposition temperature on structure and properties of the films were investigated by X-ray diffractometery, Scanning electronic microscopy, UV-visible spectrophotometer, as well as Four-point Probes System. The results revealed that moderate Al-doping and deposition temperature were helpful to improve the crystal quality and optoelectronic properties of ZnO:Al films. The lowest resistivity of 9.5×10^{-3} Ωcm and the average transmittance of 76% in the visible region was obtained for the film deposited from ZnO:2wt% Al_2O_3 target at 75□.

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1. Introduction

ZnO:Al(ZAO) transparent conductive thin films on polymer substrates are attracting more and more attention because of light in weight, easily bending and excellent resistant to impact damage except for good optical and electrical qualities [1-2]. ZAO films deposited firstly on TPT substrate by rf-sputtering magnetron at room temperature have been reported [3-4]. The structure and properties of ZAO films are influenced significantly by the processing parameters, such as the deposition temperature, Al-doping concentration, sputtering power, deposition pressure etc. The optimization of these parameters can result in high quality ZAO films with excellent electrical and optical properties [5-7]. In this paper, ZAO thin films on transparent TPT were deposited by RF-Magnetron Sputtering method. The effects of Al-doping concentration and deposition temperature on the structural, optical and electrical properties of ZAO films were investigated.

2. Experimental procedure

Firstly, the ZAO thin films were deposited on TPT substrates at 25 °C by RF magnetron sputtering system from a ZnO: 1-3 wt % Al_2O_3 target (purity: 99.99%). And then ZAO films were prepared from ZnO: 2 wt % Al_2O_3 target at various deposition temperature from 25~125 °C. The target size is Φ 60 mm×5 mm. The substrates were ultrasonically cleaned in acetone and then alcohol for 15 min respectively before they were loading into the deposition chamber. The distance between the target and substrate was about 50 mm. The sputtering power and the working pressure were maintained at 120W and 1Pa respectively. The mass flow of Ar was maintained at 20 sccm and the deposition time was 180 min. The structure properties of the ZAO films were analyzed with X-ray diffraction (XRD, X'Pert PRO, λ = 0.154 nm) using Cu-Kα radiation and Scanning electronic microscopy (SEM, FE Sirion 200). The transmittance of the films was measured by spectrophotometer (UV, Lambda 35) in the range of 300~900 nm and the electrical properties were characterized by Four-point Probes (RTS-8).

3. Results and discussion

3.1. Structure properties

Fig. 1 (a) and (b) show XRD patterns of the ZAO films deposited on TPT substrates at various Al-doping concentrations and different temperatures. Fig. 2 (a), (b) and (c) are SEM images of ZAO films with different Al-doping concentration. From Fig. 1(a) and Fig. 2, all ZAO films deposited from ZnO target with different Al_2O_3 content had a diffraction peak at 2θ about 34.0°, which is associated with the (002) plane of hexagonal phase ZnO and implies that the prepared films had a c-axis preferred orientation. The crystallinity of ZAO films was highest when the Al_2O_3 content in ZnO target was 2%, and the surface of film was uniform and smooth. From Fig. 1(b), it could be seen that the crystal quality of ZAO films was improved firstly when the deposition temperature increased from 25 ^oC to 75 ^oC, and then decreased from 75 ^oC to 125 ^oC. It was because that the energy of sputtering particles and their motilities increased with increase of deposition temperature, thus the crystallinity of ZAO films was improved. But when the deposition temperature increased further, the TPT substrates were softened, resulting in the crystallinity of ZAO films deteriorated and c-axis preferred orientation disappeared. When the deposition temperature was 75 ^oC, the (002) peak intensity of ZAO films was strongest and the grain size of ZAO film calculated by Scherrer equation [8] was largest, reached to 49.2 nm.

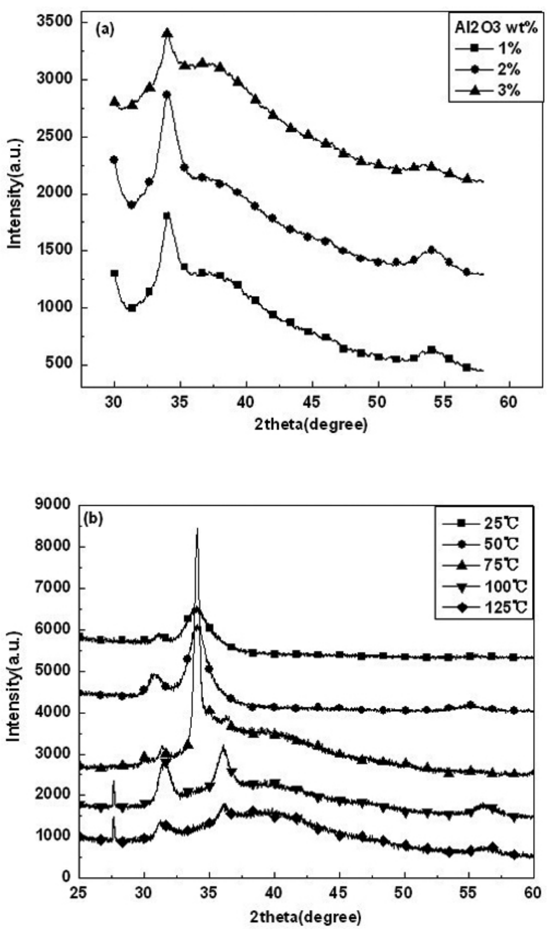

Fig. 1. XRD patterns of the ZAO films deposited on TPT substrates (a) at different Al-doping concentration; (b) at different deposition temperature.

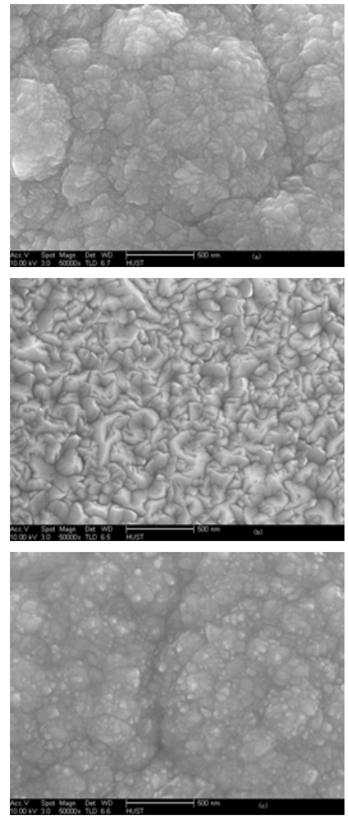

Fig. 2. SEM images of the ZAO films deposited on TPT substrates at different Al-doping concentration(a)1 wt% Al_2O_3 ;(b)2% Al_2O_3;(c)3% Al_2O_3.

3.2. Optical properties

Fig. 3(a) and (b) show the optical transmittances of the ZAO films deposited on TPT with various Al-doping concentrations and deposition temperatures respectively. Fig. 3(c) is the curve of average tranmittance and optical band gap to Al_2O_3 content in ZnO target. The transmittance of ZAO films increased as Al-doping concentration increasing. It maybe due to two reasons: the improvement of crystal quality and surface roughness, and film thickness reduction [9]. The optical band gap (E_{opt}) was calculated by Tauc equation [10]: $a(hv) = c(hv - E_{opt})^{\frac{1}{2}}$. From Fig. 3(c), the optical band gap of ZAO films was between 3.32 eV to 3.47 eV, which was larger than the band gap of un-doped ZnO (~3.3eV).The E_{opt} widened with the increase of Al-doping concentration. It can be attributed to Burstein-Moss effect [11], which results from the Pauli Exclusion Principle.

That is the bule shift of absorption edge with increasing carrier concentration. Al^{3+} constitutes Zn^{2+} in the lattice when Al_2O_3 doping in ZnO target, providing a electron for conduction band, thus carrier concentration increasing and Fermi energy level moves to conduction band, so the absorption edge moves to shorter wavelength.

The transmittance of the films on polymer was influenced obviously by the deposition temperature. The average transmittance of films prepared at 25~75 ^{o}C was over 76%, but the transmittance of the sample deposited at 100 ^{o}C and 125 ^{o}C decreased sharply and was below 55%, meaning too high deposition temperature had negative influence on the transparency of the ZAO films, it could be attributed to polymer substrate softened under high temperature, resulting in defects increasing and light scattering enhancing, so the transmittance decreased deeply.

3.3. Electrical properties

Fig. 4(a) and (b) are separately the electrical properties of the ZAO films deposited at different Al-doping concentrations and different deposition temperatures. As shown in Fig. 4(a), the moderate Al doping concentration could enhance conductivity of the films, but too much Al-doping concentration deteriorated its electrical property. It is because that the carrier concentration increases resulting from Al substituting Zn in ZnO lattice and Fermi energy level moves to conduction band, thus the conductive property increasing. But excessive Al-doping will accumulate inner ZnO films and be easy to form non-conductive Al_2O_3 structure in the grain boundary, scattering center increasing, reducing the carrier mobility, and thereby decreasing the conductivity of the ZAO films. In this experiment, the lowest resistivity of 2.3×10^{-1} Ω·cm was obtained when ZAO film was deposited from ZnO target with Al_2O_3 content of 2 wt%. From Fig. 4(b), it could be seen that the resistivity of ZAO films decreased with the increase of deposition temperature from 25 ^{o}C to 75 ^{o}C and then increased as deposition temperature increasing from 75 ^{o}C to 125 ^{o}C. The lowest resistivity was 9.5×10^{-3} Ωcm for the film deposited at 75 ^{o}C. This is related to film structure. XRD results indicated that the crystallinity of ZAO films increased as deposition temperature increasing, scattering in grain boundary decreasing and carrier mobility increasing, at the same time, higher temperature is benefit to increase Al-doping efficiency, increasing carrier concentration, thus reducing the resistivity. But too high deposition temperature will reduce oxygen vacancy and lead the Al_2O_3 accumulation in grain boundary, increasing the carrier scattering, on the other hand, the TPT substrates was softened at high temperature above 75 ^{o}C, the crystallinity decreasing, thus leading the increase of film resistivity.

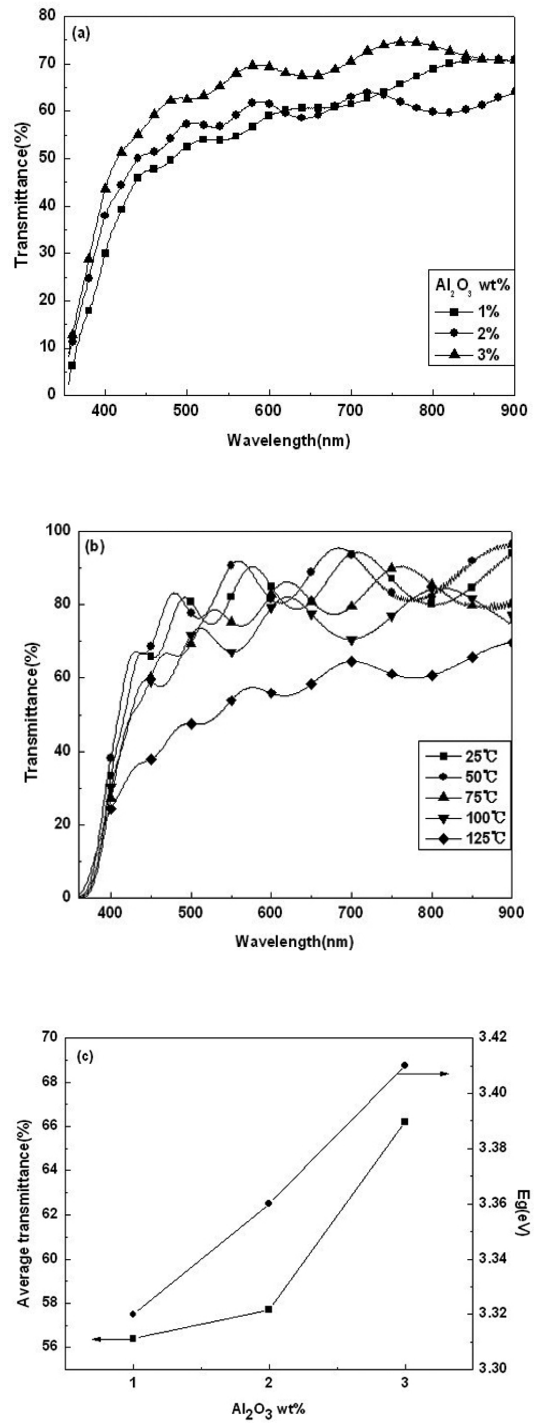

Fig. 3. Optical transmittance of the ZAO films deposited on TPT substrates (a) at different Al-doping concentration; (b) at different deposition temperature;(c) The relationship of average transmittance and optical band gap to Al_2O_3 content in ZnO target.

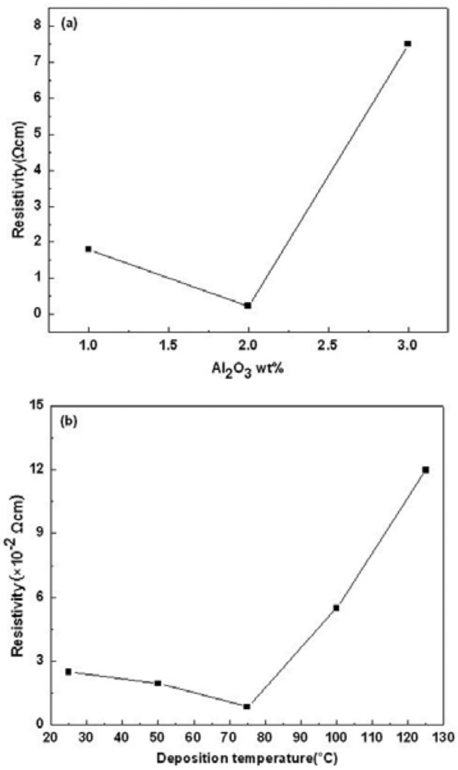

Fig. 4. Resistivity of the ZAO films deposited on TPT substrates (a) at different Al-doping concentration; (b) at different deposition temperature.

4. Conclusion remarks

ZAO thin films have been prepared on polymer substrates by RF magnetron sputtering. The effects of Al-doping concentration and deposition temperature on the structure and properties of ZAO films were identical. The moderate Al-doping and deposition temperature were of benefit to improve the crystal quality and optoelectronic properties of ZnO:Al films. A best transparency of 76% in the visible region and resistivity of 9.5×10^{-3} Ωcm were obtained for the ZnO: Al film on TPT substrate deposited from ZnO:2 wt% Al_2O_3 target at 75 °C with sputtering power and working pressure of 120 W and 1Pa.

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