

Effect of deposition times of Al₂O₃ buffer layer on the structural and optical properties of AZO film on the polyethylene terephthalate substrates

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Abstract. The aluminium-doped zinc oxide with Al₂O₃ buffer layer (AZO/Al₂O₃) films were deposited on the polyethylene terephthalate substrates by radiofrequency magnetron sputtering. Compared with the AZO films without Al₂O₃ buffer layer, the crystallite size and (002) peak of the AZO/Al₂O₃ films changed with the deposition times; the full-width at half-maximum (FWHM) of (002) peak decreases from 0 to 25 min. The effects of Al₂O₃ buffer layer on the surface morphology of AZO/Al₂O₃ and optical properties of films were investigated by SEM and UV–Vis–NIR spectrophotometer, respectively. The results reveal that the average transmittance of the AZO films in the visible wavelength region is ~90%, stronger deep level emissions centred on 550 nm is attributed to intrinsic defects in the AZO films on the organic polymer PET substrates.

Keywords. Deposition; buffer layer; optical properties; sputtering.

1. Introduction

Recent investigations showed that B-, Ga-, Al- and F-doped ZnO films present both low resistivity and high transmittance in the visible region [1–3]. Aluminium-doped zinc oxide (AZO) is regarded as an ideal substitute for the ITO due to its similar optical and electrical properties as well as its low cost, environmental stability and potential applications [4–6]. In the meantime, the development of transparent conducting films on polymer substrates make flexible devices, which show a great market prospects [7–9]. The related researches of AZO thin films on polymer were conducted, such as polyphthalamide (PPA) substrate, polycarbonate substrate (PC), polyimide (PI) substrate and polyethylene terephthalate (PET) substrate [10–13]. Among these substrate materials, PET could meet some basic requirements, such as optical transmittance, folding property, temperature compatibility and surface smoothness. It is usual practice to deposit some type of buffer layers on AZO films to enhance the crystal quality of AZO films [14]. In recent years, many researchers have tried different types of buffer layers, such as ZnO/Ag/Al-doped ZnO [15], Zn-doped SnO₂/Ag/Zn-doped SnO₂ [16] and AZO/metal/AZO [17], most of them focussed on the different effects of different buffer layers, little research focussed on the effect of Al₂O₃ buffer layer on the deposition times. However, the deposition times have a very important impact on the film thickness and substrate temperature, which are associated with thermal stress [18], furthermore, the coefficient of thermal expansion between thin films and flexible

substrate causes residual stress. Hence, the deposition times of Al₂O₃ buffer layer are an important parameter on the structural and properties of a flexible electronics.

In this article, high transmittance of AZO thin films on PET substrates was conducted using multilayer deposition technology and ceramic targets by introducing the Al₂O₃ buffer layer at room temperature. The influence of the different deposition times of Al₂O₃ buffer layer on the structural, optical properties of AZO films were investigated systematically. It could be a meaningful work to improve flexible electronic devices, such as TCO layer on LEDs, solar cells and touch panels.

2. Materials and method

AZO thin films were deposited on PET substrates using the RF-sputtering method using ZnO (99.99% purity) target, Al₂O₃ (99.99% purity) target and AZO (ZnO:Al₂O₃ 98:2 wt%) target, respectively. The distance between the target and substrates was about 60 mm. The target was pre-sputtered for 10 min to remove the impurities. Film thickness was 380–450 nm (determined with a surface roughness detector DEKTAK), All the films were deposited by RF sputtering on PET at room temperature. X-ray diffraction (XRD) was obtained using a Rigaku Dymax equipment with a CuK α monochromatic radiation operated at 50 kV and 300 mA. The electrical resistivity was measured using the Van der Pauw method. The surface microstructure was examined using a scanning electron microscope (SEM). The optical

transmittance of AZO films was measured using UV–VIS spectrophotometer (725PC) and Raman spectrometer.

3. Results and discussion

XRD patterns of the AZO films (figure 1) show a preferred (002) orientation and a hexagonal wurtzite structure. It can be concluded that the buffer layers of Al₂O₃ seem to have no influence on the preferred orientation, the intensity of the peak (002) increases and moves into the small angle direction with the addition of Al₂O₃ buffer layer (20 min), this implies that the buffer layer of Al₂O₃ improved the quality of the AZO films and increased interplanar spacing at the same time. Different from the substrates of glass, silicon and sapphire, the PET substrate is easy to produce plastic deformation during

the process of deposition, which increases the lattice constant; this result is consistent with Mass [19]. Except the characteristic peak of the PET and ZnO, no other characteristic peaks, such as Al or Al₂O₃ were observed. This result indicates that there is no other phase generated and that Al was incorporated into ZnO lattice.

Figure 2a shows the XRD for the Al₂O₃ buffer layer deposited with time in the range of 5–25 min, it is obvious to observe that all films exhibit a strong (002) preferred orientation at ~34.2°, which is close to the value of criterion ZnO crystal. With the increase in deposited time of Al₂O₃ buffer layer, the intensity of peak (002) increases at the beginning and decreases after it reaches a maximum value at deposited time of 20 min, the peaks (002) located at 34.26, 34.28, 34.32, 33.97, 33.97 and 33.97° (0, 5, 10, 15, 20 and 25 min), respectively. Compared to AZO films without Al₂O₃ buffer layer, the peak (002) moves into the direction of large angle with Al₂O₃ buffer layer's increasing deposited time, however, when deposited time of Al₂O₃ buffer layer continues to increase (15, 20 and 25 min), the slight deviation to lower angles of the (002) diffraction from 34.32° indicates that tensile lattice strain exists in the film along *c*-axis direction, and then the angles of the (002) diffraction keep no change at the same angle at 33.97°. According to Bragg equations as equation (1):

$$2d \sin \theta = \lambda, \tag{1}$$

when the deposition time of Al₂O₃ buffer layer increases from 0 to 15 min, the temperature increases, and subsequent elastic deformation of cooling substrates make the AZO thin films, showing compressive stress, cause interplanar spacing *d* to smaller. However, when the deposition time of Al₂O₃ buffer layer continues to increase from 15 to 25 min, the temperature increases as well, the temperature of PET substrate reach a critical value, which leads to the PET elastic deformation

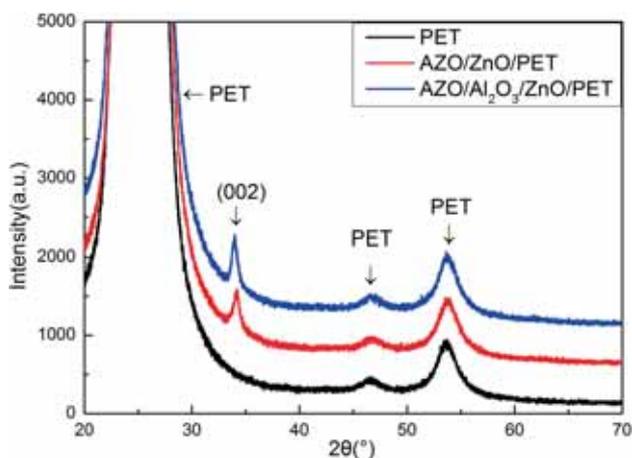


Figure 1. XRD patterns of AZO thin films on different substrates.

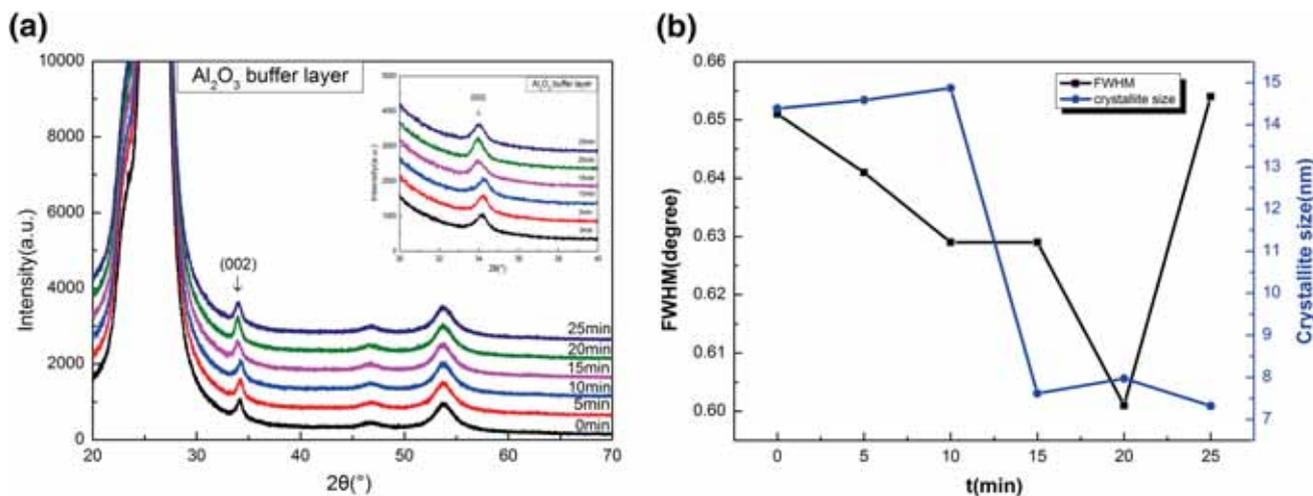


Figure 2. (a) XRD patterns of AZO thin films on the Al₂O₃ buffer layer grown at different times. (b) FWHM and crystallite size of AZO thin films on the Al₂O₃ buffer layer grown at different times.

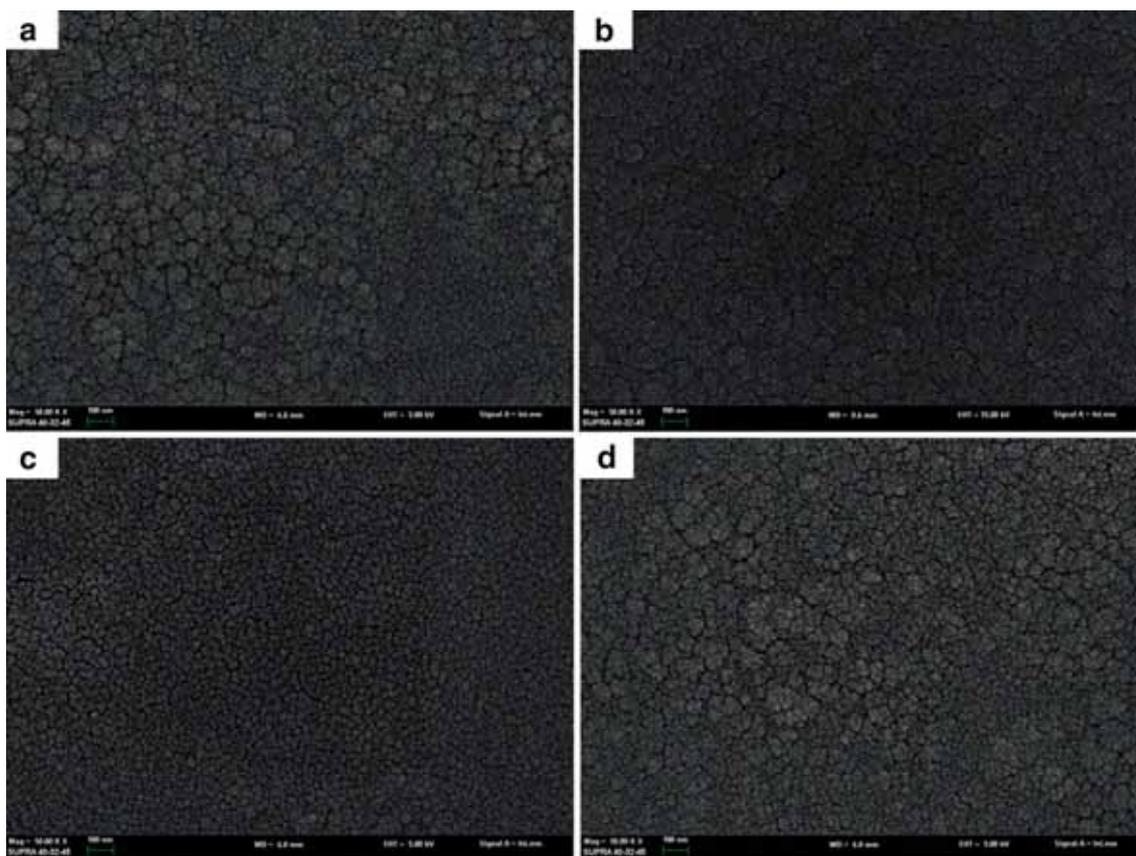


Figure 3. Scanning electron microscopy image of AZO films with Al₂O₃ buffer layer at various sputtering times (a: 0, b: 10, c: 20 and d: 25 min).

weaker or disappear, interplanar spacing becomes bigger and keeps no change at the same value. Figure 2b is FWHM and crystallite size of Al₂O₃ buffer layer grown at different times, the average crystallite sizes were calculated by Scherrer equations as equation (2):

$$D = 0.9\lambda / B \cos \theta. \tag{2}$$

As shown in figure 2b, when deposited time continues to raise from 0 to 20 min, the intensity of peaks (002) increased and the FWHM decreased slightly. It is considered that the difference in aluminium and zinc atoms radii leads to decrease in crystallite size. From figure 2a and b, we can conclude that when Al₂O₃ buffer layer deposited time is 20 min, the AZO film shows a minimal FWHM and moderate grain size, which is related to better AZO film quality.

Figure 3 shows SEM image of AZO films with Al₂O₃ buffer layer at various sputtering times. It is found that the deposition time of buffer layer has a significant impact on the surface morphologies of AZO films. The morphology of AZO/Al₂O₃ film deposited at 20 min is found to be compact and continuous (figure 3c). Compared with the PET substrates without Al₂O₃ buffer layer (figure 3a), the Al₂O₃ buffer layer compensated partial performance of the

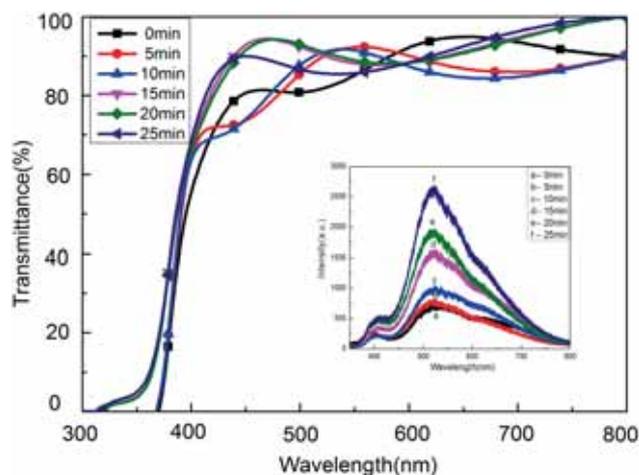


Figure 4. Transmission and photoluminescence spectra of the AZO films with Al₂O₃ at various sputtering times.

PET substrates, such as temperature-resistance and surface smoothness, which might contribute to improve the crystalline quality and optical properties of AZO on it. Moreover, with the increase in the deposition time, the sputtered particles could have higher energy to self-diffuse at slightly higher substrate

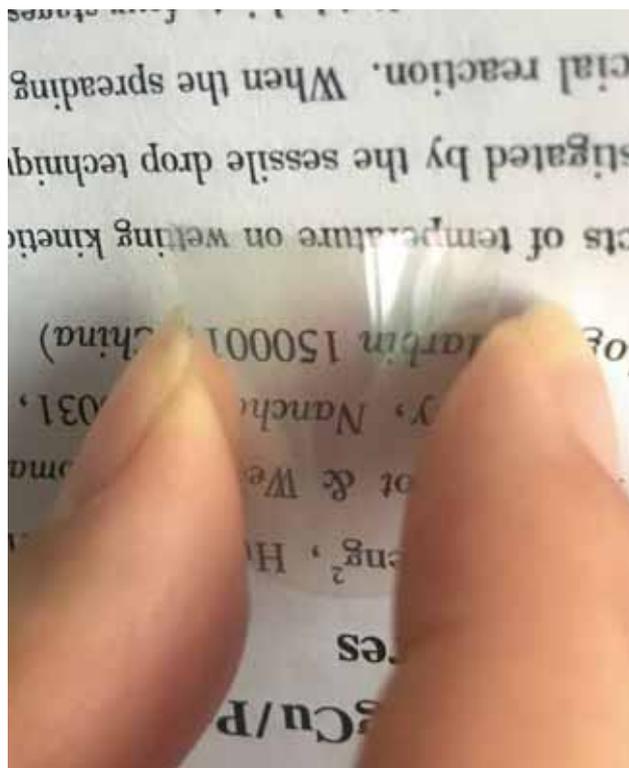


Figure 5. Flexible and transparent AZO/Al₂O₃ film deposited on PET substrate.

temperatures, which results in the densification and uniform of the AZO films. However, further increase of the deposition time to 25 min leads to a deterioration of the AZO films (figure 3d); it is considered that the difference of thermal expansion coefficient between PET and Al₂O₃ damages the adhesion of the Al₂O₃ buffer layer in the growth process. The grain size of the AZO films with the addition of Al₂O₃ buffer layer decreased, and the longer deposited time (20 min)

of the Al₂O₃ buffer layer, the smaller grain size of the AZO films. Because the radius of Zn²⁺ and Al³⁺ are 72 and 53 pm, respectively [20], the length of lattice along *c*-axis direction is expected to be smaller when Al atoms instead of Zn atoms in the crystal. This point may be also related to the minimization of the surface free energy during the nucleation stage [21].

The optical transmittance of AZO thin films and Al₂O₃/PET thin films are shown in figure 4, which indicated that average transmittance of the films is ~90% in the visible region. The transmission window and the transmittance remain unchanged almost, although its deposition time increased from 0 to 25 min. Different deposition times just show slight impact on transmittance. Figure 5 shows the flexible and transparent AZO film prepared by sputtering at PET substrate (bend substrate), the thickness of the AZO and Al₂O₃ layers are 380 and 50 nm separately. Insert in figure 4 shows the PL spectra of AZO films deposited at various times from 0 to 25 min. The deep level emissions centred on 550 nm in the green range are very strong in this experiment, however, the intense UV emission with very slight or without deep-level emission were observed from the AZO films on the glass substrates [22]. It is due to the organic polymer PET substrate presents weaker binding force with AZO/Al₂O₃ thin films compared with glass substrate, which leads to increase in intrinsic defects in the AZO films.

Figure 6 shows the resistivity, Hall mobility and carrier concentration of AZO films deposited at various times. The resistivity of AZO films reduced from 0 to 20 min as increase in Al₂O₃ buffer layer. The optimal resistivity was $1.2 \times 10^{-4} \Omega\text{cm}$ at 20 min. As shown in figure 5, the Hall mobility and carrier concentration increased at the beginning and decreased after it reached a maximum value at deposited time of 20 min. These results may be due to the addition of Al₂O₃ buffer layer, Al as donor atoms caused the increase of carrier concentration. At the same time, the existence of compressive residual stress suppresses the increase in the Hall mobility.

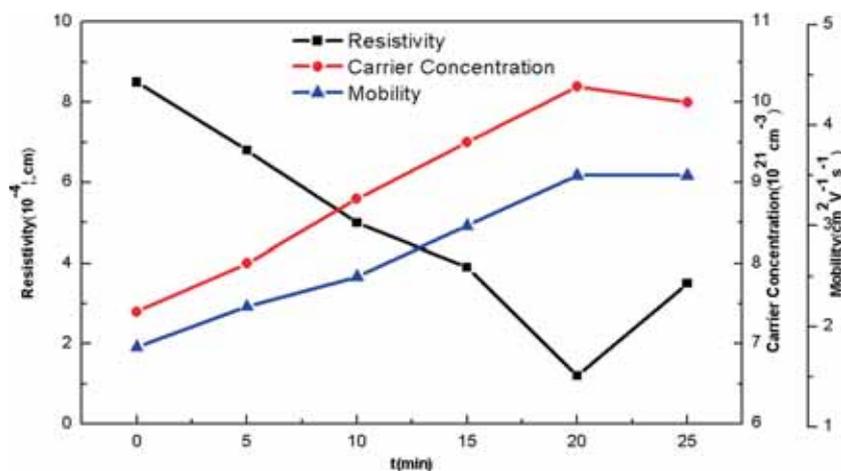


Figure 6. Variations of resistivity, mobility and carrier concentration of the AZO films with Al₂O₃ at various sputtering times.

While the deposited time of Al_2O_3 buffer layer reached 25 min, the O exist in Al_2O_3 prevents the movement of electrons and leads to higher resistivity.

4. Conclusions

High transparent conductive AZO/ZnO films and AZO/ Al_2O_3 /ZnO films were prepared on PET substrates by RF sputtering at room temperature, the structural and optical properties of AZO/ZnO films and AZO/ Al_2O_3 /ZnO films were analysed systematically. Addition of the buffer layer of Al_2O_3 did not change the preferred orientation and enhanced the crystal quality of AZO films on PET substrates. The effect of deposition times of Al_2O_3 buffer layer provides a reference for the applications of the AZO/ Al_2O_3 films on flexible optoelectronics.

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