Effects of the ZnO buffer layer and Al proportion on AZO film properties*

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To evaluate the influence of the ZnO buffer layer and Al proportion on the properties of ZnO: Al (AZO)/ZnO bi-layer films, a series of AZO/ZnO films are deposited on the quartz substrates by electron beam evaporation. The X-ray diffraction measurement shows that the crystal quality of the films is improved with the increase of the film thickness. The electrical properties of the films are investigated. The carrier concentration and Hall mobility both increase with the increase of buffer layer thickness. However, the resistivity reaches the lowest at about 50 nm-thick buffer layer. The lowest resistivity and the maximum Hall mobility are both obtained at 1 wt% Al concentration. But the optical transmittance of all the films is greater than 80% regardless of the buffer layer thickness with Al concentration lower than 5 wt% in the visible region.
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Doped ZnO films have been recognized as a potential candidate to the industry standard tin-doped indium oxide (ITO). Doping small amount of Ⅲ and Ⅶ elements, such as B, Al, Ga and F[1-6], into ZnO results in a remarkable decrease in the electrical resistivity. On the other hand, the optical transparency in the visible region remains high. Among these, Al-doped ZnO (AZO) films have been widely studied and are considered as promising materials for ITO. In addition, there are also several technologies used for preparing such films, such as spay pyrolysis[7], chemical vapor deposition[8], pulsed laser ablation[9], direct-current and radio-frequency (RF) magnetron sputtering[10,11], atomic layer deposition (ALD)[12], etc.

Commonly, the ZnO films deposited on *c*-plane sapphire have high residual carrier concentrations, and show a rough surface morphology due to the large lattice mismatch and large difference in the thermal expansion coefficient between ZnO and sapphire[13]. Nowadays, some attempts have been made to solve the significant effect of growth conditions on the physical properties of the films by inserting buffer layer between the film and substrate. Shin et al[14] reported that the electrical properties of the GZO thin film which was grown on Al_2O_3 substrate were improved by introduction of a ZnO buffer layer. Zhang et al[15] researched the effect of ZnO buffer layer on the crystallinity and electrical properties of the AZO/GZO bi-layer thin films deposited on *c*-sapphire substrate. In this paper, high performance AZO/ZnO bi-layer films are grown on the quartz glass substrates by electron beam evaporation, and the effects of buffer layer on the structural, electrical and optical properties of the bi-layer thin films are discussed in detail.

The AZO transparent conducting films with or without ZnO buffer layer were deposited onto quartz glass substrates by electron beam evaporation technology. The ceramic targets were synthesized from high purity ZnO (99.99% purity) and Al_2O_3 (99.9% purity) powder. A series of targets with Al proportions of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% were prepared, respectively. Before deposition, quartz glass substrates were ultrasonically and chemically cleaned in alcohol and deionized water, and then blow-dried with nitrogen. Afterwards, they were mounted on a holder with diameter of 100 mm at the right of the target surfaces with the target-substrate distance of 10 cm.

Prior to the deposition, the chamber was evacuated to a background pressure lower than 2.0×10^{-3} Pa, and the target was pre-sputtered for 5 min to remove the impurities on the target surface. The growth pressure during the film deposition maintained in the range from 7.5×10^{-3} Pa to 9.5×10^{-3} Pa. Meanwhile the substrate temperature was 200 °C. The AZO deposition time was kept as 20 min. The X'Pert PRO X-ray diffraction (XRD) spectrometer was used to analyze the structural properties using Cu Kα radiation. The electrical

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resistivity, carrier concentration and Hall mobility of the deposited films were obtained by Hall effect measure system using the Van der Pauw configuration with a HL5500 apparatus in which indium electrodes are used for Ohmic contacts. The optical transmittances of the films were performed with ultraviolet/visible/near-infrared (UV/VIS/NIR) spectrophotometer from 300 nm to 800 nm.

As shown in the inset of Fig.1, the samples possess the structure of AZO/ZnO/quartz. Fig.1 illustrates the relationship between ZnO buffer layer thickness and deposition time. The thicknesses of ZnO buffer layer films deposited for 20 min, 30 min and 40 min are 35 nm, 52 nm and 70 nm, respectively. It can be seen that in our experiment the thickness of the buffer layer increases approximately linearly with the deposition time, keeping a growth rate of 1.75 nm/min.

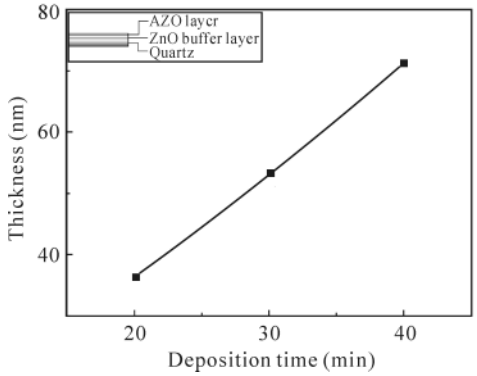

Fig.1 Relationship between buffer layer thickness and deposition time

Fig.2 shows typical XRD patterns of the AZO/ZnO films with the buffer layer deposition time of 0 min, 20 min, 30 min and 40 min, respectively. The Al proportion of AZO layer is 2 wt%, and the deposition time is 20 min. The measurements were taken on the central region of the samples. It can be easily found that the insertion of ZnO buffer layer indeed improves the crystalline quality. As well known in Fig.2, all the samples show the (002) preferred orientation regardless of the buffer layer deposition time, and they are located around $2\theta = 34.4^{o}$, which is very close to that of the standard ZnO crystal. The very weak (100) and (101) peaks also appear in the film with buffer deposition time of 40 min. It can be seen from Fig.2, with the increase of the buffer deposition time, the (002) peak intensity increases too. The full width at half maximum (FWHM) of the (002) peak decreases at the same time. The fact that there is no impure phase, such as Al_2O_3, appearing indicates that the doped Al replaces Zn in the lattice, achieving a good doping.

Fig.3 illustrates the electrical properties of the bi-layer films on the quartz glass substrates as a function of the buffer deposition time. From Fig.3(c), it can be easily seen that the

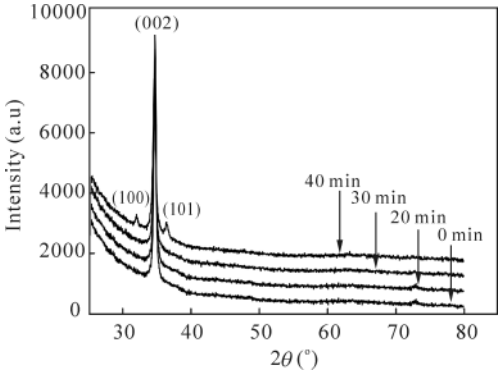

Fig.2 XRD patterns of AZO/ZnO bi-layer films with different buffer deposition time

resistivity initially decreases and then increases with the increase of the buffer deposition time from 0 to 40 min, and the minimum resistivity value of $2.506 \times 10^{-3}\ \Omega$·cm is obtained at 30 min. From Fig.3(a) and (b), we can see that the trend of carrier concentration n is nearly the same as that of the Hall mobility μ. The Hall mobility describes a nearly linear increase distribution. Maximum values of carrier concentration about 3.21×10^{20} cm^{-3} and mobility about 9.58 cm^2/V·s are both attained at 40 min. In conclusion, the film with excellent electrical properties can be got when the buffer deposition time keeps at 30 min, which means the buffer thickness is 50 nm or so.

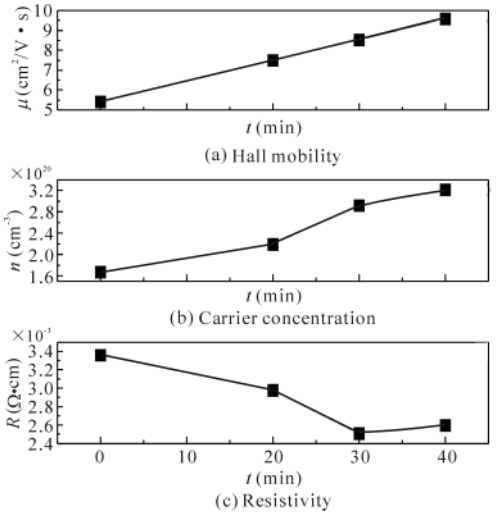

Fig.3 Electrical properties of AZO/ZnO bi-layer films with different buffer deposition time

Based on the above results, a set of samples with identical buffer deposition time of 30 min by varying Al proportion were consequently prepared to evaluate their electrical properties, and the results are shown in Fig.4. As Al proportion increases, the resistivity decreases at first. When it reaches the lowest value of $1.807 \times 10^{-3}\ \Omega$·cm at 1wt% Al proportion,

it increases rapidly. Meanwhile, the Hall mobility shows even an opposite trend. Its maximum value of 14.6 $cm^2/V·s$ is also obtained at 1 wt% Al concentration. At this situation, the carrier concentration is lightly lower than its maximum value. No matter the Al concentration increases or decreases, its resistivity increases. This phenomenon can be explained as the doping of Al can cause the increase of free electron and carrier concentration, which results in the decrease of resistivity. However, when the amount of Al reaches a certain value, Al gathering at the grain boundaries becomes blockage preventing the movement of free electron, and then the mobility of free electron decreases.

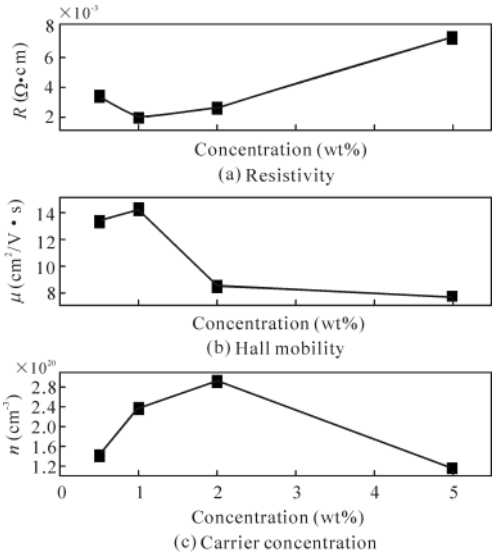

Fig.4 Electrical properties of AZO/ZnO bi-layer films with different Al concentrations

So we can make a conclusion that the preparation parameters to obtain excellent electrical properties of films are the buffer deposition time of 30 min and the Al concentration of 1 wt%.

The optical transmittances of the bi-layer films as a function of buffer deposition time and Al concentration are shown in Figs.5 and 6, respectively. In the former, the 2 wt% Al proportion AZO layer films were deposited for 20 min, and the buffer deposition time was changed from 0 to 40 min. In the latter, the buffer layer films were deposited for 30 min and the AZO layer was deposited for 20 min, with the Al proportion changing from 0.5 wt% to 5 wt%. All of the samples show a very similar transmittance in the entire range in both Figs.5 and 6. The average transmittance in 400−800 nm is between 80% and 90%, which indicates the high crystal quality of our films. It is found that not only the optical transmittance of these films is not decreased by increasing the buffer deposition time from 0 to 30 min or by increasing the Al concentration from 0.5 wt% to 2 wt%, but also the bi-layer films provide an excellent shield to UV light. This characteristic can be understood from the fact that the AZO or ZnO is a direct band-gap semiconductor with an energy gap of about 3.2 eV. It is remarkable that the optical transmittance of the film at 5 wt% Al concentration declines sharply.

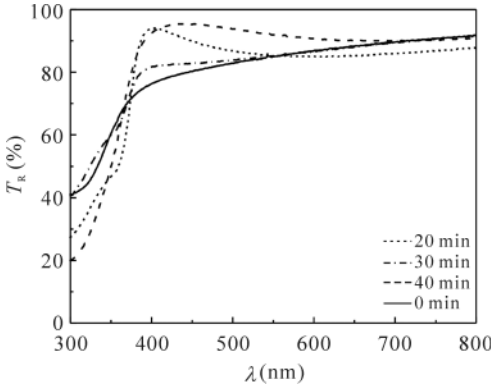

Fig.5 Optical transmittances of AZO/ZnO bi-layer films with different buffer deposition time

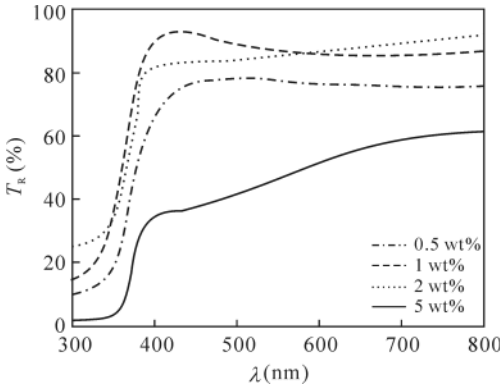

Fig.6 Optical transmittances of AZO/ZnO bi-layer films with different Al proportions

In summary, high-quality AZO/ZnO bi-layer films are prepared on quartz substrates at growth pressure of 7.5×10^{-3} − 9.5×10^{-3} Pa and substrate temperature of 200 °C. It is found that by inserting ZnO buffer layer, the characteristics of AZO films are indeed improved, including the crystal and optoelectronic properties. All the films are highly along the *c*-axis which is perpendicular to the substrate surface. Meanwhile, the crystal quality of AZO films is significantly improved with the increase of the buffer layer thickness. By the introduction of ZnO buffer layer with a thickness less than 50 nm between the AZO film and substrate, both the carrier concentration and Hall mobility increase, and the resistivity of bi-layer films is lower than that of single layered AZO films. With the same buffer layer thickness, the minimum resistivity can be attained at 1 wt% Al proportion. Thus, the preparation parameters are the buffer thickness of about 50 nm

and the Al concentration of 1 wt%, and in this case the films with excellent electrical properties can be attained.

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