Effect of substrate temperature on the properties of deep ultraviolet transparent conductive ITO/Ga_2O_3 films*

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Abstract: ITO/Ga_2O_3 bi-layer films were deposited on quartz glass substrates by magnetron sputtering. The effect of substrate temperature on the structure, surface morphology, optical and electrical properties of ITO/Ga_2O_3 films was investigated by an X-ray diffractometer, a scanning electron microscope, a double beam spectrophotometer and the Hall system, respectively. The structural characteristics showed a dependence on substrate temperature. The resistivity of the films varied from 6.71×10^{-3} to 1.91×10^{-3} Ω·cm as the substrate temperature increased from 100 to 350 ℃. ITO (22 nm)/Ga_2O_3 (50 nm) films deposited at 300 ℃ exhibited a low sheet resistance of 373.3 Ω/□ and high deep ultraviolet transmittance of 78.97% at the wavelength of 300 nm.

Key words: transparent conductive film; bi-layer films; deep ultraviolet; magnetron sputtering; gallium oxide; indium tin oxide

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1. Introduction

Conventional transparent conductive oxides (TCOs), such as indium tin oxide (ITO) and Al-doped zinc oxide (AZO), are opaque in the deep ultraviolet region (< 300 nm) due to a small band gap (~ 3.2 eV). The applications of deep ultraviolet TCOs is increasing in the fields of lithography, sterilization, transparent electrodes, optoelectronic devices and so on[1, 2]. New TCO materials need to be explored for this purpose. β-Ga_2O_3 is a TCO with a optical band gap of 4.9 eV that exhibits deep ultraviolet transparency as well as good electric conductivity when dopants are introduced[3]. The conductivity of ~ 1 S/cm was first attained in polycrystalline β-Ga_2O_3 films deposited at 880 ℃ on silica glass by pulse laser deposition (PLD) method[4]. The maximum conductivity obtained so far was 8.2 S/cm by preparing tin-doped β-Ga_2O_3 films[5].

For the purpose of improving the electrical properties of deep ultraviolet transparent conductive films, the ITO/Ga_2O_3 bi-layer films were prepared by magnetron sputtering. We successfully obtain both low sheet resistance and high optical transmittance in the deep ultraviolet region. The effects of substrate temperature on the structure, surface morphology, optical and electrical properties of ITO/Ga_2O_3 films were studied.

2. Experimental

ITO/Ga_2O_3 bi-layer films were deposited on quartz glass substrates by radio frequency (RF) magnetron sputtering of Ga_2O_3 ceramic targets (purity of 99.99%) and direct current (DC) magnetron sputtering of ITO targets (purity of 99.99%, $In_2O_3 : SnO_2 = 90 : 10$ wt%). The quartz glass substrates were ultrasonically cleaned and dried in flowing nitrogen gas. The sputtering chamber was pumped down to 6×10^{-4} Pa before introducing argon gas. The sputtering was carried out under a pressure of 0.5 Pa in pure argon atmosphere with a target-to-substrate distance of 60 mm. The temperature was controlled by a feedback controlled heater and measured by a thermocouple gauge. Substrate temperature was controlled in the range of 100–350 ℃. The thicknesses of Ga_2O_3 layer and ITO layer were 50 nm and 22 nm respectively.

The crystallinity and crystal orientation were determined by using an X-ray diffractometer (XRD) with Cu-Kα radiation. The surface morphology was analyzed using a field effect scanning electron microscope (SEM). The optical transmission was measured in the range of 200–850 nm by using a double beam spectrophotometer. The resistivity ρ, free carrier concentration n and hall mobility $\mu_{\rm H}$ were determined by using the Vander Pauw method at a constant magnetic field of 0.517 T.

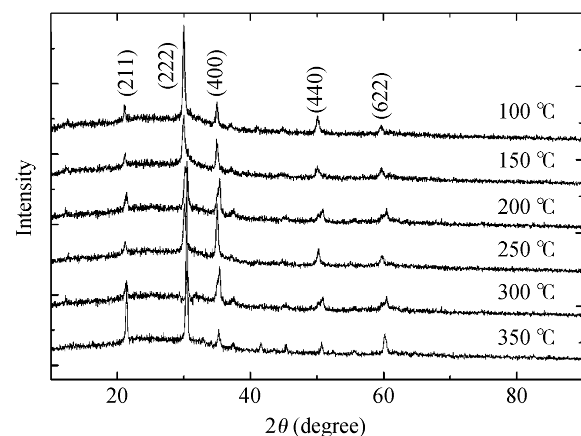

Fig. 1. XRD patterns of ITO (150 nm)/Ga_2O_3 (150 nm) films deposited at different substrate temperatures.

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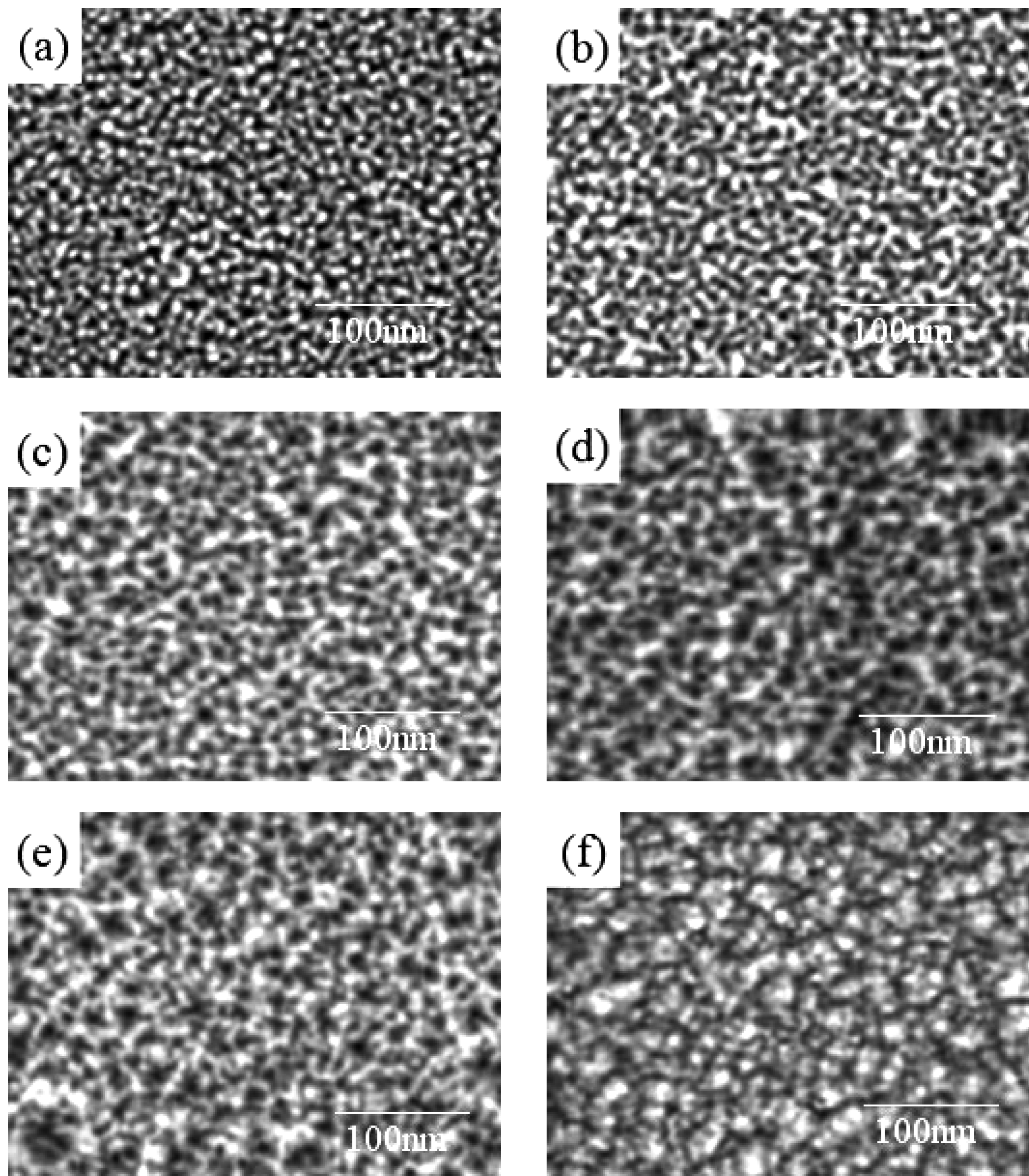

Fig. 2. SEM surface photographs of ITO/Ga_2O_3 films deposited at different substrate temperatures. (a) 100 ℃. (b) 150 ℃. (c) 200 ℃. (d) 250 ℃. (e) 300 ℃. (f) 350 ℃.

3. Results and discussion

3.1. Structural and morphological properties

The diffraction information of ITO (22 nm)/Ga_2O_3 (50 nm) films was covered by that of the glass substrate. Ga_2O_3 and ITO layers, both 150 nm thick, were prepared for the XRD measurement. XRD patterns of ITO (150 nm)/Ga_2O_3 (150 nm) films deposited at different substrate temperatures are shown in Fig. 1. The Ga_2O_3 layers are all amorphous and ITO layers are polycrystalline. The growth orientation of ITO layers are (211), (222), (400), (440) and (622), corresponding to the cubic structure of the In_2O_3[6]. The film deposited at 100 ℃ has a strong (222) diffraction peak, indicating a preferred orientation along [111] direction. The film prepared at 250 ℃ shows strong (400) diffraction peak, which suggests a preferred orientation along [100] direction. The variation of the orientation from [111] to [100] is related to the energy of the sputtered particles reaching the substrate surface[7].

As the substrate temperature increases from 250 to 350 ℃, the (400) peak intensity decreases, whereas the (222) peak intensity increases. The film deposited at 350 ℃ shows a strong (222) diffraction peak. The change in orientation from [100] to [111] is related to the high deposit rate[8].

Figure 2 shows the surface morphology of ITO/Ga_2O_3 films deposited at different substrate temperatures. The morphology of ITO/Ga_2O_3 films changes with increasing substrate temperature. At low temperature, the films are formed by clusters of nanocrystals separated by voids. The size of the crystalline grains and the compactness of the films increase as the substrate temperature increases.

3.2. Optical properties

Transmittance spectra in both visible and deep-UV regions for ITO/Ga_2O_3 films prepared at different substrate tempera-

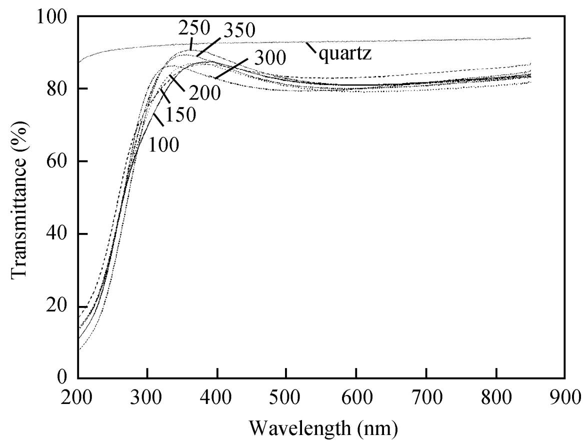

Fig. 3. Transmittance spectra of ITO (22 nm)/Ga_2O_3 (50 nm) films deposited at different substrate temperatures.

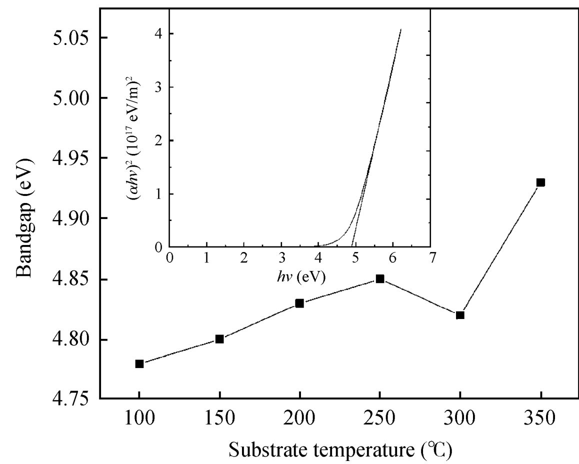

Fig. 4. Variation of optical band gap of ITO (22 nm)/Ga_2O_3 (50 nm) films with substrate temperatures. Insert shows a typical plot of $h\nu$ versus $(\alpha h\nu)^2$ for ITO/Ga_2O_3 films deposited at 250 ℃.

tures are shown in Fig. 3. The transmittance of quartz substrate without coating is also shown in Fig. 3. The average transmission in the deep-UV region (280–300 nm) is greater than 65%. Transmission of ITO/Ga_2O_3 films deposited at 300 ℃ is 78.97% at 300 nm wavelength.

All the samples have high transmittance at 300–400 nm because of the antireflective effect. At normal incidence, reflectance occurs mainly at the front surface of the ITO layer and the back surface of the Ga_2O_3 layer because the refractive indices of the ITO layers and Ga_2O_3 layers have approximately the same value. As the bi-layer films have an appropriate thickness, the light beams reflected from the front surface of the ITO layer and back surface of the Ga_2O_3 layer are of opposite phase and of nearly equal amplitude, resulting in destructive interference and diminishing reflective light[9].

The variation in the transmission peak intensity can be related to the film structure and surface morphology. A rise in substrate temperature promotes growth of some orientation grains but inhibits some others. The difference in the grain sizes of the films deposited at different substrate temperatures are shown in Fig. 2. The grains of the films gradually become larger when the substrate temperature increases from 100 to 250 ℃. Whereas the grains of the film deposited at 300 ℃ are smaller, they become larger when the substrate temperature is as high as 350 ℃. These results are consistent and correlate well with those of XRD patterns shown in Fig. 1. When the substrate temperature increases from 100 to 250 ℃, the (222) diffraction peak intensity of the films gradually decreases, but the (400) diffraction peak intensity increases. The average grain size of the film increases, leading to the increase of the optical transmission peak intensity from 87.32% to 91.97%. A dramatic drop appears in the (222) diffraction peak intensity of the film deposited at 300 ℃. The average grain size and transmission peak intensity (85.28%) of the film decrease. The average grain size and transmission peak intensity (89.79%) increases as the film deposited at 350 ℃ has a stronger (222) diffraction peak and a sharp (211) peak.

Figure 4 shows the effect of substrate temperature on the optical band gap of the ITO (22 nm)/Ga_2O_3 (50 nm) films. The optical band gap of the ITO/Ga_2O_3 films is estimated from $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where α is the absorption coefficient, A is

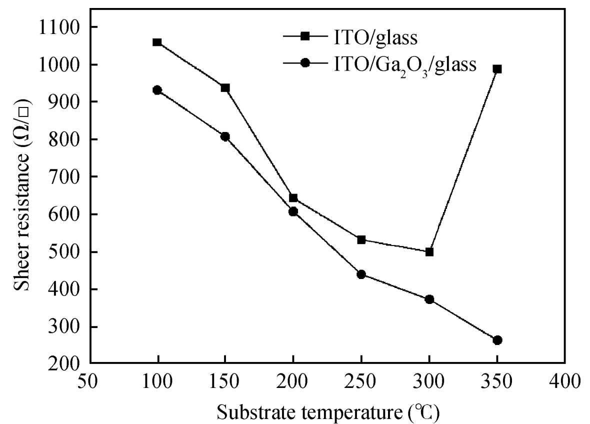

Fig. 5. Sheet resistance of ITO (22 nm) films and ITO (22 nm)/Ga_2O_3 (50 nm) films as a function of substrate temperature.

a constant, E_g is the optical band gap, and $h\nu$ is the photon energy[10]. According to $(\alpha h\nu)^2 = A^2(h\nu - E_g)$, the intersection on the $h\nu$ axis from the plot of $(\alpha h\nu)^2$ versus $h\nu$ in the linear region gives the optical band gap of the films[11].

The optical band gap of the ITO/Ga_2O_3 films varies with substrate temperature. The change of optical band gap is mainly due to the change of the carrier concentration. The band gap of the ITO/Ga_2O_3 film increases from 4.78 to 4.85 eV as the substrate temperature increases from 100 to 250 ℃. The optical band gap is 4.82 eV at 300 ℃ substrate temperature and 4.93 eV at 350 ℃ substrate temperature. This effect can be interpreted as the Burstein–Moss (B–M) shift, which is due to electrons filling to a higher energy state near the bottom of the conduction band. We can write $E_g = E_{g0} + \Delta E_g^{\text{B-M}}$, where E_{g0} is the intrinsic band gap and $\Delta E_g^{\text{B-M}}$ is the B–M shift due to the filling of low lying levels in the conduction band[12]. An expression for the B–M shift is given by $\Delta E_g^{\text{B-M}} = (h^2/8\pi^2 m_{vc}^*)(3\pi^2 n)^{2/3}$, where n is the carrier concentration, m_{vc}^* is the reduced effective mass of the carriers. From this expression it is clear that B–M shift is directly proportional to $n^{2/3}$.

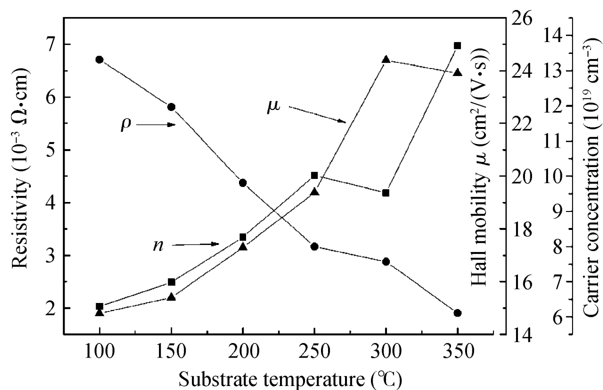

Fig. 6. Variation of resistivity (ρ), carrier concentration (n) and Hall mobility (μ) of ITO (22 nm)/Ga_2O_3 (50 nm) films with substrate temperature.

3.3. Electrical properties

Figure 5 shows the variations of sheet resistance of ITO/glass and ITO/Ga_2O_3/glass deposited at different substrate temperatures. The sheet resistance of ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer films are smaller than that of ITO (20 nm) monolayer films at the same temperature. The sheet resistance of ITO (22 nm) monolayer film decreases with rising substrate temperature, with a minimum value of 499.8 Ω/□ at 300 ℃, and then increases to 989.7 Ω/□ at 350 ℃. This increase may be due to the contamination of the films by alkali ions from the glass substrate. The sheet resistance of ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer film decreases from 930.9 to 264.5 Ω/□ as the substrate temperature increases from 100 to 350 ℃. The sheet resistance of ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer film is 373.3 Ω/□ at the temperature of 300 ℃.

Figure 6 shows the resistivity, carrier concentration and Hall mobility of ITO (22 nm)/Ga_2O_3 (50 nm) films as functions of substrate temperature. The resistivity of ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer films decreases from 6.71×10^{-3} to 1.91×10^{-3} Ω·cm as the substrate temperature increases from 100 to 350 ℃. The resistivity depends on the carrier concentration and Hall mobility. Grain boundaries and scattering centers are the significantly influencing factors of the mobility[13, 14]. Crystallographic defects, such as grain boundaries, dislocations, interstitials and vacancies, induce the scattering of carriers, which make carriers inactive[15]. The films deposited at low temperature are nanocrystalline, whose formation is due to the limited mobility of the adatoms at low substrate temperature, as indicated in Figs. 2(a)–2(c). When the substrate temperature increases to higher temperature, the sputtered particles have enough energy to diffuse, which may result in the formation of a more compact films. At 350 ℃, the impurity in Ga_2O_3 layer may diffuse into ITO films, degrading the Hall mobility.

The variation in the Hall mobility can be related to the film structure. As shown in Figs. 1 and 6, the Hall mobility increases as the peak intensity ratio of (400) to (222) is increased with substrate temperature ranging from 100 to 300 ℃, the Hall mobility decreases as the ratio of (400) to (222) is decreased when substrate temperature increases from 300 to 350 ℃. The mobility of the charge carrier in ITO/Ga_2O_3 films is related to two scattering mechanism: ionized-impurity scattering and grain boundary scattering. If we consider that the grain boundary scattering is the dominant factor as discussed by Wu *et al.*[16], it can be suggested that the possibility of the carrier, which is scattered by grains oriented in the [100] direction, is smaller than that by grains oriented in the [111] direction.

The free carriers in ITO/Ga_2O_3 films are provided by the oxygen vacancies and the substitution of Sn^{4+} for In^{3+}. The increase of carrier concentration from 100 to 250 ℃ may be due to the diffusion of Sn atoms from interstitial location and grain boundaries into the In cation sites. Since the Sn atom has a valency of 4 and In is trivalent, the Sn atoms act as donors in ITO films. Hence the increase in Sn diffusion, caused by the rising substrate temperature, can result in higher electron concentration. However, a higher substrate temperature (> 250 ℃), which is favorable for stoichiometric indium oxides and gallium oxides, can lead to the disappearance of oxygen vacancy in ITO films and Ga_2O_3 films. Therefore the carrier concentration has a slight drop from 250 to 300 ℃. When the temperature is above 300 ℃, the impurity Sn in the Ga_2O_3 layer may diffuse into the ITO films, which increases the carrier concentration.

4. Conclusions

ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer films with low sheet resistance of 373.3 Ω/□ and high transmittance of 78.97% at the wavelength of 300 nm were obtained under a substrate temperature of 300 ℃. The film's structure, the growth preferential orientation and the optical band gap change with increasing substrate temperature. The sheet resistance of ITO (22 nm)/Ga_2O_3 (50 nm) bi-layer film is superior to that of ITO (22 nm) monolayer film at the same deposition temperature. The resistivity of ITO (22 nm)/Ga_2O_3 (50 nm) film decreases with increasing substrate temperature.

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