Electrical and optical properties of deep ultraviolet transparent conductive Ga_2O_3/ITO films by magnetron sputtering*

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Abstract: Ga_2O_3/ITO films were prepared by magnetron sputtering on quartz glass substrates. The transmittance and sheet resistance of ITO films and Ga_2O_3/ITO films were measured by using a double beam spectrophotometer and four point probes. The effect of the ITO layer and Ga_2O_3 layer thickness on the electrical and optical properties of Ga_2O_3/ITO bi-layer films were investigated in detail. Ga_2O_3 (50 nm)/ITO (23 nm) films exhibited a low sheet resistance of 323 Ω/□ and high deep ultraviolet transmittance of 77.6% at a wavelength of 280 nm. The ITO layer controls the ultraviolet transmittance and sheet resistance of Ga_2O_3/ITO films. The Ga_2O_3 layer thickness has a marked effect on the transmission spectral shape of Ga_2O_3/ITO films in the violet spectral region.

Key words: transparent conductive film; deep ultraviolet; gallium oxide; indium tin oxide
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1. Introduction

A need for deep ultraviolet transparent conductive oxides (TCOs) has recently emerged for use in the fields of lithography, surface modification, anion generation, sterilization and so on[1]. Conventional TCOs, such as ITO and ZnO, are opaque in the deep ultraviolet region (< 300 nm) due to a small band gap (∼3.2 eV). New TCO materials need to be explored for this purpose. The difficulties of creating deep ultraviolet transparent thin films are as follows. Firstly, the position (scaled from the vacuum level) of the conduction band bottom is relatively high, so the donor levels tend to become deep levels. Secondly, introduction of the shallow donor levels into the compounds for the efficient release of electrons into the conduction band is more difficult than in narrow gap oxides[2]. This significantly reduces the number of candidate materials for deep ultraviolet transparent TCO. The β-Ga_2O_3 is considered to be a good candidate because this material has a large band gap of 5 eV. The crystal structure of β-Ga_2O_3 belongs to the monoclinic system with the lattice parameters of a = 1.223 nm, b = 0.304 nm, c = 0.580 nm and β = 103.7° and the space group of C2/m, in which Ga^{3+} ions occupy both octahedral and tetrahedral sites. The conductivity of ∼1 S/cm was first attained in polycrystalline β-Ga_2O_3 films by PLD method deposited at 880 ℃ on silica glass[3]. The maximum conductivity obtained so far is 8.2 S/cm(about1.22×10^4 Ω/□) by preparing $(\bar{2}01)$ oriented tin-doped β-Ga_2O_3 films, which was sufficiently high for applications such as antistatic coatings over photo masks for lithography processes[1]. However, a higher conductivity is desirable for applications that need large electric currents, such as ultraviolet transparent electrodes for ultraviolet light emitting diodes. Many techniques have been employed to prepare the Ga_2O_3 films, such as chemical vapor deposition[4], spray pyrolysis process[5], sol–gel processes[6], pulsed laser deposition[7] and sputtering[8]. In this paper, we propose new transparent conductive films having the bi-layer structure of Ga_2O_3/ITO prepared by a magnetron sputtering method. We could successfully obtain the characteristics of both low sheet resistance and high optical transmittance in the deep ultraviolet region.

2. Experimental procedure

ITO thin films and Ga_2O_3/ITO bi-layer films were deposited on quartz glass substrates by radio frequency magnetron sputtering Ga_2O_3 ceramic targets (purity of 99.99%) and direct current magnetron sputtering ITO targets (purity of 99.99%, In_2O_3 : SnO_2 = 90 : 10 wt.%). The quartz glass substrates were ultrasonically cleaned in acetone, alcohol, rinsed in deionized water and subsequently dried in flowing nitrogen gas. The sputtering was carried out at a pressure of 0.5 Pa in a pure argon atmosphere with a target-to-substrate distance of 60 mm. The sputtering chamber was pumped down to 6×10^{-4} Pa before introducing the argon gas. The rotation speed of the substrate was 18 rpm. The substrate temperature was measured using a thermocouple gauge. The temperature was controlled using a feedback controlled heater. The variation in the substrate temperature during deposition was maintained within ±1 ℃. The substrate temperature was controlled in the range of 25–350 ℃. Sheet resistance was measured by the four point probe method. Film thickness was measured using a stylus profiler. Surface morphology was observed by a field emission scanning electron microscope. Optical transmission was measured in the range of 200–800 nm using a double beam spectrophotometer by discounting the quartz substrates.

3. Results and discussion

Figure 1 shows the transmittance spectra of ITO films deposited at different substrate temperatures in the range from

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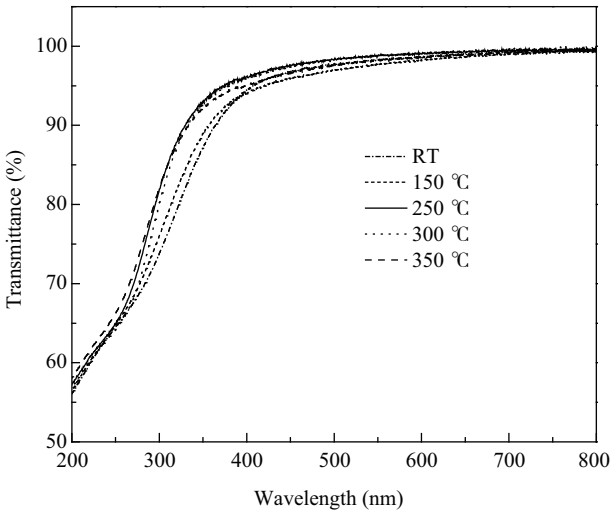

Fig. 1. Transmittance spectra of ITO films deposited at different substrate temperatures.

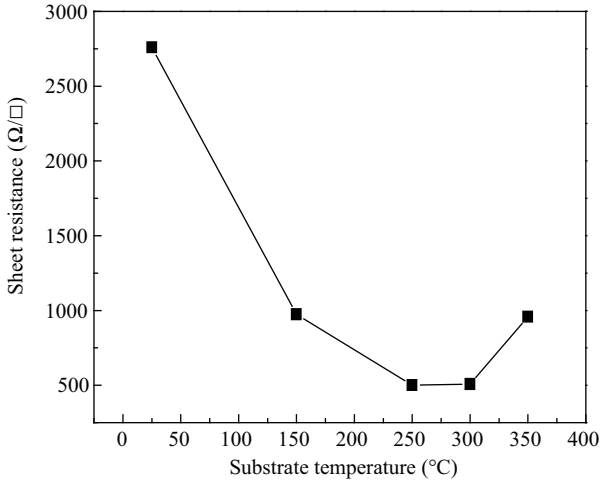

Fig. 2. Dependence of sheet resistance of ITO films on substrate temperatures.

200 to 800 nm. The thickness of ITO films was 23 nm. ITO films exhibit a large average transmittance of over 95% in the visible range and a novel characteristic of transparency in the deep ultraviolet region. The absorption edge shifts to shorter wavelengths gradually with the increase in substrate temperature from room temperature to 250 ℃. This means that the band gap of ITO films increases with substrate temperature. The increase in band gap is due to an increase in carrier concentration with substrate temperature[9]. The increase in band gap with carrier concentration can be explained on the basis of the Burstein–Moss effect. Assuming that the conduction band and valence band are parabolic in nature and that the B–M shift is the predominant effect, we can write $E_{\rm g} = E_{\rm g0} + \Delta E_{\rm g}^{\rm B-M}$, where $E_{\rm g0}$ is the intrinsic band gap and $\Delta E_{\rm g}^{\rm B-M}$ is the B–M shift due to the filling of low lying levels in the conduction band[10]. An expression for the B–M shift is given by $\Delta E_{\rm g}^{\rm B-M} = (h/8\pi^2 m_{\rm vc}^*)(3\pi^2 n)^{2/3}$, where n is the carrier concentration and $m_{\rm vc}^*$ is the reduced effective mass of the carriers. From this expression it is clear that the B–M shift is directly proportional to $n^{2/3}$. When the substrate temperature is higher than 250 ℃, the carrier concentration of uncontaminated ITO films may also be improved. However, the contaminated ITO layer near the interface is enhanced with the increase in substrate temperature, and the carrier concentration of contaminated ITO films may be decreased. So a change in carrier concentration of ITO films is not significant. According to the Burstein–Moss theory, the B–M shift $\Delta E_{\rm g}^{\rm B-M}$ is not obvious, and the absorption edge shifts slightly when the temperature is higher than 250 ℃.

Variation in the sheet resistance with substrate temperature is shown in Fig. 2. The sheet resistance decreases with an increase in substrate temperature and becomes a minimum value of 501 Ω/□ at a temperature of 250 ℃, and then increases with further increases in substrate temperature. The crystallinity of the ITO films grows better with an increase in substrate temperature, causing an increase in mobility. The diffusion of Sn atoms from interstitial locations and grain boundaries into the In cation sites increases with an increase in substrate temperature. Since the Sn atom has a valency of 4 and In is trivalent,

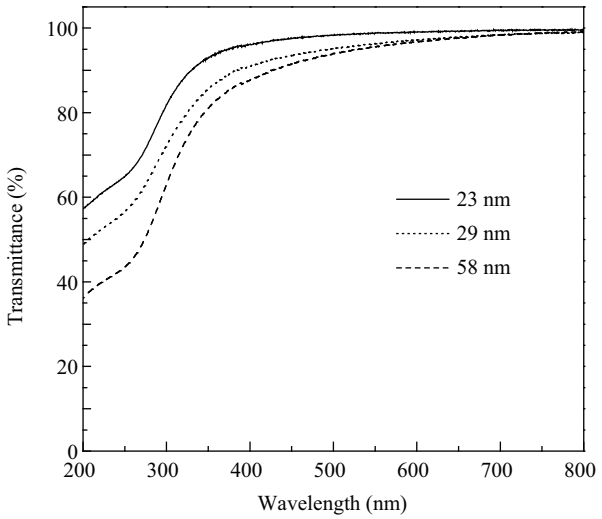

Fig. 3. Transmittance spectra of ITO films with different thicknesses.

the Sn atoms act as donors in ITO films. Hence the increase in Sn diffusion with substrate temperature results in a higher carrier concentration. The decrease in sheet resistance with an increase in substrate temperature is attributed to the increase in the mobility and carrier concentration. When the substrate is higher than 250 ℃, the dead layer near the interface due to contamination is enhanced, resulting in decreased mobility and increased sheet resistance[11].

The optical properties of ITO films deposited at 250 ℃ have been analyzed as a function of the film thickness. Figure 3 shows the transmittance spectra of ITO films with thicknesses ranging from 23 to 58 nm. The average transmittance of the films in the visible range is over 90% by discounting the quartz substrates. With the increase in thickness, the transmittance of ITO films decreases in the entire optical spectra region and the absorption edge shifts to a longer wavelength. The absorption coefficient of ITO films is near zero in the near infrared region, and the absorption coefficient increases nonlinearly from visible to deep ultraviolet region[12]. All the ITO films suffer little absorption in the near infrared region and strong absorption in

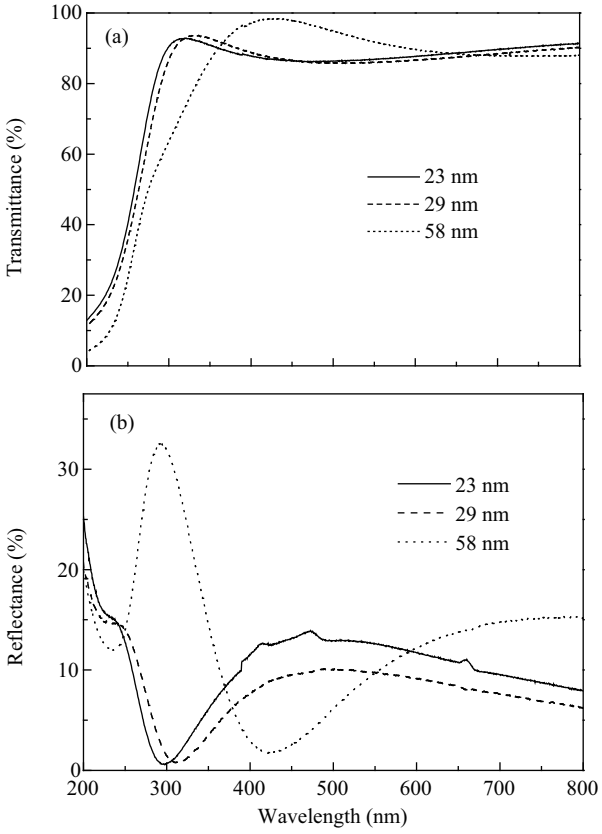

Fig. 4. (a) Transmittance and (b) reflectance spectra of Ga_2O_3 (50 nm)/ITO films with different ITO layer thicknesses.

the deep ultraviolet region, and different ITO films have bigger absorption differences in the deep ultraviolet region due to the thickness effect. As the surface roughness increases with the film thickness, surface scattering is slightly enhanced. The transmittance of ITO films with thickness in the entire optical spectra region is determined by the absorption and reflection of ITO films.

Figure 4 shows the dependence of the transmittance spectra and reflectance spectra of Ga_2O_3 (50 nm)/ITO films on ITO layer thickness varying from 23 to 58 nm. Ga_2O_3 (50 nm)/ITO films were deposited at a temperature of 250 ℃. The average transmittance of the films is over 85% in the visible range. The onset of absorption is shifted to longer wavelengths as the ITO thickness increases. Comparing the transmittance properties of ITO films and Ga_2O_3 (50 nm)/ITO films, Ga_2O_3 (50 nm)/ITO films show higher transmittance at 280 nm wavelength for different ITO layer thicknesses. Ga_2O_3 (50 nm)/ITO films with ITO thickness of 23 nm, 29 nm and 58 nm have higher transmittance around 310 nm, 330 nm and 420 nm, respectively. This is ascribed to the antireflective effect shown in Fig. 4(b). The wavelength position difference between transmittance crest and reflectance trough for Ga_2O_3 (50 nm)/ITO films is ascribed to absorption effects. At normal incidence, reflectance occurs mainly at the front surface of the ITO layers and the back surface of the Ga_2O_3 layers because the refractive indices of the ITO layer and Ga_2O_3 layer have approximately the same value. For the ITO layers with appropriate thickness, the light beams reflected on the front surface of the ITO layers and back surface of the Ga_2O_3 layers are of opposite phase

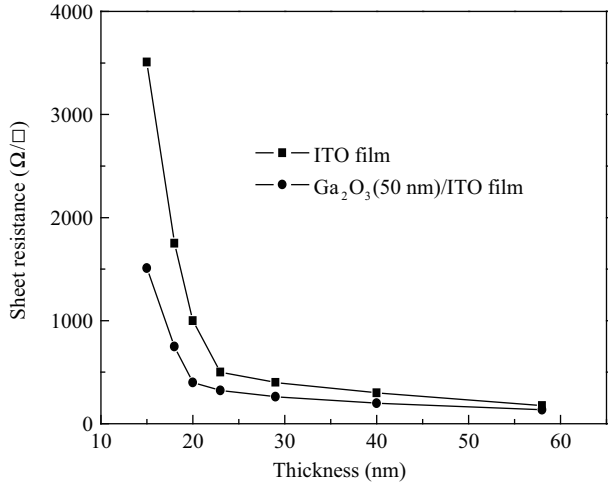

Fig. 5. Dependence of sheet resistance of ITO films and Ga_2O_3 (50 nm)/ITO films on ITO layer thickness.

and of nearly equal amplitude, which leads to destructive interference and the reflective light is induced to diminish. The transmittance of the Ga_2O_3/ITO film in the deep ultraviolet region strongly depends upon the ITO layer thickness. The optical gap E_g of the film can be obtained by plotting $(\alpha h\nu)^2$–$h\nu$ and extrapolating the straight line portion of this plot to the energy axis. E_g for the Ga_2O_3 (50 nm)/ITO (23 nm), Ga_2O_3 (50 nm)/ITO (29 nm), Ga_2O_3 (50 nm)/ITO (58 nm) film is 4.91, 4.9 and 4.86 eV, respectively.

Figure 5 shows the sheet resistance of ITO films and Ga_2O_3 (50 nm)/ITO films with different ITO layer thicknesses. The thickness of the ITO layer varies from 15 to 58 nm. The sheet resistance of the ITO films and Ga_2O_3 (50 nm)/ITO films decreases as the ITO film thickness increases. The ITO film resistance is 3508 Ω/□and the Ga_2O_3 (50 nm)/ITO film resistance is 1509 Ω/□ for an ITO layer thickness of 15 nm. Starting with thin ITO films, it is also seen that the sheet resistance drops sharply with increasing ITO thickness. This behavior changes drastically at approximately 23 nm ITO thickness for ITO films and approximately 20 nm ITO thickness for Ga_2O_3 (50 nm)/ITO films. Then, a slow drop in the sheet resistance is also observed. This behavior is attributed to a transition from the formation of distinct islands to a continuous film. To observe the initial growth behaviors of ITO film, they were deposited on the substrate covered with 50 nm thick Ga_2O_3 film with deposition times of 15 and 37 s. The growth rate of ITO films was 0.48 nm/s under these conditions. The initial morphologies of the ITO films are shown in Fig. 6. For the film deposited for 15 s, the nucleation process has ended and nucleus growth has already begun. And thus an island structure has appeared (Fig. 6(a)). For the film deposited for 37 s, the islands connected to each other and a coalescence phenomenon with channels was observed. The resistance of the film deposited for 15 s was beyond the measurable range of the instrument, and that of the film deposited for 37 s was 750 Ω/□ due to the connection of the islands. The sheet resistance of 23 nm ITO film and Ga_2O_3 (50 nm)/ITO (23 nm) film is as low as 501 Ω/□ and 323 Ω/□, respectively. The sheet resistance of Ga_2O_3 (50 nm)/ITO films is lower than that of ITO films with the same ITO thickness. The ITO layer controls the sheet resistance of

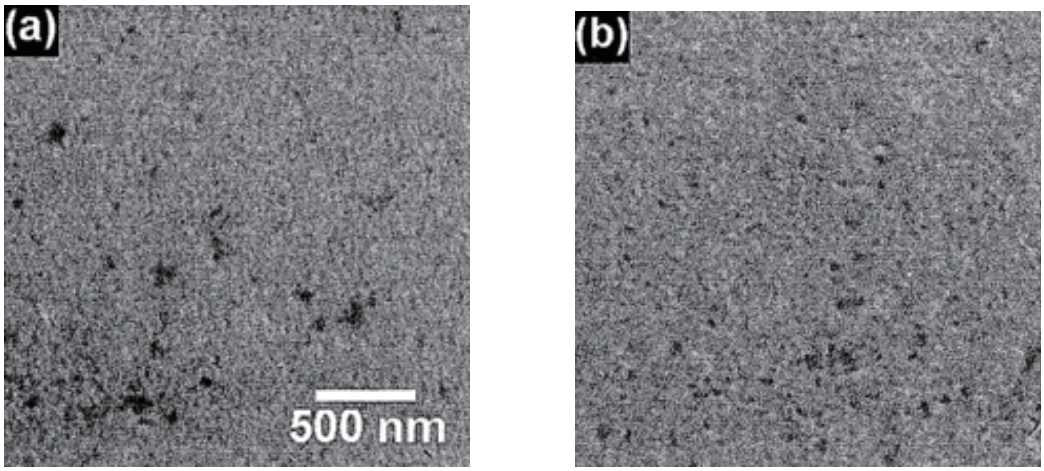

Fig. 6. SEM micrographs of Ga_2O_3 (50 nm)/ITO films with different deposition times of the ITO film. (a) 15 s. (b) 37 s.

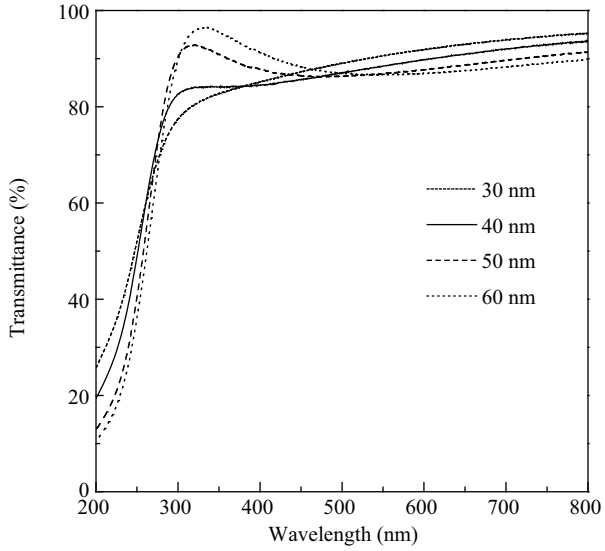

Fig. 7. Dependence of transmittance spectra of Ga_2O_3/ITO (23 nm) films on Ga_2O_3 layer thickness.

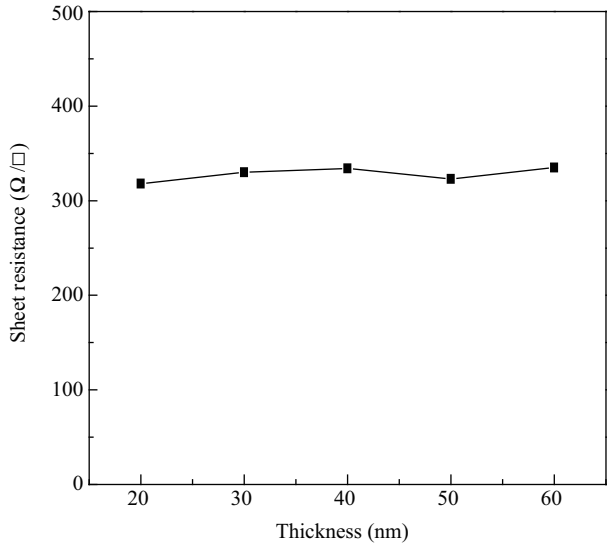

Fig. 8. Dependence of sheet resistance of Ga_2O_3/ITO (23 nm) films on Ga_2O_3 layer thickness.

Ga_2O_3/ITO films. Although the Ga_2O_3(50 nm)/ITO (58 nm) film has a low resistance of 135 Ω/□, it suffers from low optical transmittance in the deep ultraviolet region. Transmittance spectra of Ga_2O_3/ITO (23 nm) films deposited at 250 ℃ with different Ga_2O_3 layer thickness are shown in Fig. 7. The thickness of the Ga_2O_3 layer was varied from 30 to 60 nm. The absorption edge shifts slightly to longer wavelength with increasing Ga_2O_3 layer thickness. For the thickness of Ga_2O_3 layers above 30 nm, the peak of transmittance is observed. This is because the light beams reflected on the front surface of the ITO layers and the back surface of the Ga_2O_3 layers are of opposite phase and of nearly equal amplitude, which leads to destructive interference and the reflective light is induced to diminish. The Ga_2O_3 (50 nm)/ITO (23 nm) film exhibits a larger transmittance than other films at wavelengths from 277 to 300 nm. The Ga_2O_3 (50 nm)/ITO (23 nm) film shows high transmittance of 90.4% at a wavelength of 300 nm and 77.6% at a wavelength of 280 nm. The optical gap E_g of the Ga_2O_3 (30 nm)/ITO (23 nm), Ga_2O_3 (40 nm)/ITO (23 nm), Ga_2O_3 (50 nm)/ITO (23 nm) and Ga_2O_3 (60 nm)/ITO (23 nm) films is 4.98, 4.94, 4.9 and 4.85 eV, respectively. The sheet resistance of Ga_2O_3/ITO (23 nm) films for different thicknesses of Ga_2O_3 layer is presented in Fig. 8. The sheet resistance of Ga_2O_3/ITO (23 nm) films varies slightly with increasing Ga_2O_3 layer thickness. Ga_2O_3 has very high resistance, while ITO is a good conductive semiconductor. The sheet resistance of the Ga_2O_3/ITO (23 nm) films largely depended on the ITO layer. The Ga_2O_3 undercoat affects the crystalline morphology of the ITO layer and has little effect on the electrical properties of the ITO layer. The Ga_2O_3 layer thickness has a significant effect on the transmission spectral shape in the violet spectral region and a slight effect on the sheet resistance of the bi-layer films.

4. Conclusions

Ga_2O_3/ITO bi-layer films having a low sheet resistance of 323 Ω/□ and a high transmittance of 77.6% at a wavelength of 280 nm were successfully deposited on quartz glass by simulta-

neous RF magnetron sputtering Ga_2O_3 ceramic targets and DC magnetron sputtering ITO targets at a substrate temperature of 250 ℃. Low resistance and good optical transmittance were obtained for ITO films deposited at a 250 ℃ substrate temperature using pure argon as the sputtering gas. The ITO layer was found to control the ultraviolet transmittance and sheet resistance of the Ga_2O_3/ITO films. The electrical property of Ga_2O_3/ITO films is superior to that of ITO films. The Ga_2O_3 layer thickness has a significant effect on the transmission spectral shape in the violet spectral region and a slight effect on the sheet resistance of bi-layer films. The Ga_2O_3/ITO films are useful as transparent electrodes for ultraviolet optoelectronic devices.

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