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Improved ITO thin films with a thin ZnO buffer layer by sputtering

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Abstract

In this paper, we report a buffering method of improving the quality of ITO thin films on glass by r.f. magnetron sputtering. By applying a ZnO buffer before the ITO deposition in the same run of sputtering, ITO films showed single (111)-oriented highly textured structure, while ITO films showed mixed-oriented polycrystalline structure on bare glass. A design of experiment was taken out to minimize the resistivity of ITO films in the deposition parameter space (oxygen ratio, total gas pressure, and temperature). Resistance measurements showed that the ITO films with ZnO buffers had a remarkable 50% decrease of resistivity comparing to those without ZnO buffers at optimized deposition condition. Room-temperature Hall effect measurements showed that the decrease in resistivity comes from a large increase of mobility and a slight increase of carrier density after forming gas annealing. The ZnO/glass may be a good alternative substrate to bare glass for producing high quality ITO films for advanced electro-optic applications. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Indium tin oxide; Resistivity; Sputtering; Zinc oxide

1. Introduction

Tin-doped indium oxide (ITO) is an *n*-type wide band-gap semiconductor. It is ubiquitous in all kinds of flat panel displays and solar cells, and it is commercially available. The resistivity of commercially available ITO deposited on glass is in the range of 6×10^{-4} Ω cm. With the progress of flat panel display technology, much lower resistivity (more fine lines) is needed to decrease the voltage drop and power consumption of ITO lines. More conductive ITO films are always preferred for such applications.

The low resistivity of ITO film is believed to be due to the large free carrier density, which is in the range of $10^{20}/cm^3$ to $10^{21}/cm^3$. It is generally accepted that these free carriers are generated by two mechanisms: (1) Sn atom substitution of In atom and giving out one extra electron, and (2) oxygen vacancies acting as two electron donors [1]. Due to its complicate crystal structure (80 atoms in an In_2O_3 unit cell [2]), the conducting mechanism of ITO is still not fully understood.

ITO thin films used commercially are mostly amorphous. There are always some interests in growing crystalline ITO films because of scientific curiosity as well as for practical reasons. It is evident to argue that increasing the ITO crystallinity is one way to increase the free carrier concentration since, with a more crystalline structure, there will be less grain boundary scattering, and Sn will have an enhanced solid solubility in the In_2O_3 matrix.

Attempts have been made to grow well-oriented ITO films without large grain boundaries on MgO and yttrium-stabilized zirconia (YSZ) [3–5]. Indeed, ITO films with increased conductivity were obtained with increased crystallinity as shown by Taga et al. [5]. The best crystalline ITO film was grown on a YSZ substrate by us with an X-ray rocking curve as narrow as 0.08° [6]. This is due to the lattice mismatch of In_2O_3 and YSZ being only 2%. The highly crystalline ITO on YSZ should find applications in opto-electronics. But, at least for the time being, all these crystalline substrates are expensive in price, are unavailable in large sizes, and are not suitable for large-size flat-panel display applications.

As an alternative to crystalline substrates, we also have investigated before the possibility of obtaining highly textured ITO films on glass by pulsed laser deposition [6]. This method involves using ZnO as a buffer layer. Very good textured ITO films can be grown on glass with a thin ZnO buffer. Yi et al. proposed that it is due to a small lattice mismatch (3%) between the neighboring oxygen–oxygen

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(O–O) distance on the closest-packed (111) plane of ITO and (0001) plane of ZnO [7].

ZnO is an interesting material in that it has a preferential growth on the *c*-axis. It is transparent and conductive (conductive or not depends on the oxygen content during sputtering). And quite recently, ZnO was found to be a good buffer layer for the growth of gallium nitride, and a room-temperature lasing material (Ref. [8] and references therein). As a transparent conducting oxide, ZnO is highly compatible with ITO in commercial production. We shall show in this paper that indeed very good quality ITO films in terms of crystallinity and resistivity can be grown on ZnO-buffered glass.

2. Experimental details

The ITO and ZnO films were deposited by r.f. magnetron sputtering. The equipment used was from Denton Vacuum, Inc. (model DVI SJ/24 LL). It has a turbo-mechanical two-stage pumped chamber with load-lock, and can be pumped to a vacuum of 10^{-7} Torr. The ITO and ZnO targets used, both of the purity of 99.9%, were commercially available hot-pressed and sintered targets. The ITO ceramic target contained 10 wt.% of SnO_2. The glass substrates used were commercial ITO glass with ITO etched away by HCl/HNO_3 dilute solutions. After etching of the ITO films, the glass substrates were rinsed in DI water and baked dry at 80°C.

For a complete experimental sequence of depositing ITO on ZnO-buffered glass, the sputtering chamber was first pumped to a base vacuum of 10^{-7} Torr. A ZnO buffer was deposited prior to ITO deposition (the condition for ZnO buffer deposition was the same for all samples). The substrate was heated to 300°C, and the chamber was back-filled with a mixture of Ar and O_2, in which the oxygen ratio (the ratio of oxygen partial pressure to total gas pressure) was kept at 10% for all ZnO buffer sputtering. The ZnO was usually deposited at a thickness of 500–800 Å. After ZnO buffer deposition, the chamber was re-pumped to at least 10^{-6} Torr, and backfilled to a desired pressure with a certain oxygen ratio. Substrate was heated to a desired temperature. Then the ITO film was deposited at a thickness of 1000–2000 Å. The actual thickness depended on the total gas pressure during sputtering. After deposition, the samples were kept at forming gas and depositing temperature for half an hour before they were taken out from the chamber. Forming gas annealing was not carried out for some samples for comparison purposes. All results and discussions presented are with forming gas annealing unless otherwise mentioned.

For ITO film deposited on glass without the ZnO buffer, the process was exactly the same except the ZnO process was omitted. All samples were deposited with substrate rotation in order to have a good surface morphology. Table 1 lists all the sputtering conditions for both ZnO buffer and ITO film. In Table 1, the r.f. powers were 100 W for ZnO deposition and 180 W for ITO deposition, which correspond to power densities of 5.1 and 9.2 W/cm^2, respectively.

Table 1
Deposition parameters for ZnO buffer and ITO film by r.f. magnetron sputtering.

Deposition parameter	ZnO buffer	ITO film
RF power (W)	100	180
Total gas pressure (mTorr)	10	5–20
Oxygen ratio (%)	10	0–3.33
Substrate temperature (°C)	300	50–300

After deposition, samples were characterized by X-ray diffraction (XRD) measurement, four-point probe resistance measurement, room-temperature Hall effect measurement, and visible spectrometry. The film thickness was measured through a surface profiler with a pattern of the film.

3. Results and discussion

3.1. Property of ZnO buffer

The purpose of ZnO buffer is to obtain textured ITO film. The requirements of ZnO buffers are that, they need to be single *c*-axis oriented (highly textured) and electrically insulating (not to interfere electric characterization of ITO). In our experiment, we found that ZnO film showed highly preferential *c*-axis growth. All our ZnO samples by sputtering deposited at various temperatures (100–300°C), oxygen ratios (1–10%), and total gas pressures (5–20 mTorr) were single *c*-axis oriented. The major factor in the control of the crystal quality of ZnO film was the temperature. The higher the temperature, the better the crystal quality (by comparing the XRD intensity of (0002) peak). So a 300°C substrate temperature was chosen. The electric property was controlled simply by the oxygen ratio. Electrically insulating ZnO was obtained by relatively higher oxygen ratio (10% used). The crystal quality and electric property of ZnO film did not show any dependence of total gas pressure in our experiment. A total gas pressure of 10 mTorr was chosen for depositing ZnO buffers.

Crystal quality and electric property of ZnO buffers were characterized by XRD and four-point probe resistance measurement. ZnO buffers of 500–800 Å thick were used for depositing ITO in this experiment. Fig. 1 shows the XRD data of a 800-Å-thick ZnO buffer deposited at substrate temperature of 300°C, total gas pressure of 10 mTorr, and oxygen ratio of 10%. It can be seen that only (0002) peak appears. According to the Scherrer equation [9],

$$t = \frac{0.89\lambda}{\beta\cos\theta} \tag{1}$$

where t is the crystal size, λ is the wavelength of the X-ray,

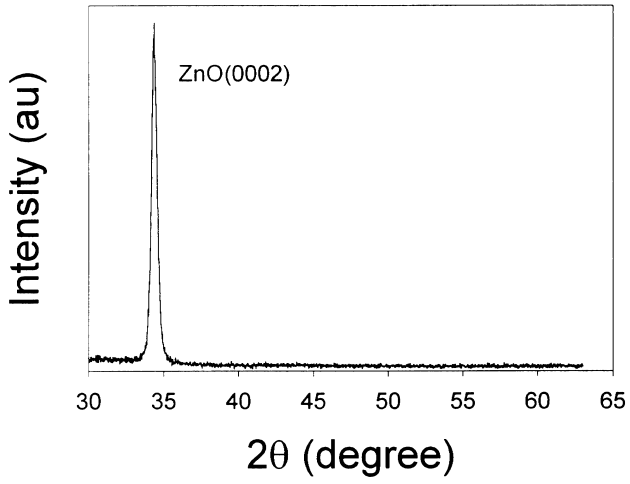

Fig. 1. XRD curve of a 1000 Å ZnO film grown on glass at 300°C, 10 mTorr total pressure with an oxygen ratio of 10%.

which is 1.540562 Å for K_α line of Cu used in our experiment, θ is the diffraction angle ($\theta = 17.21°$ for (0002) plane of ZnO), β is the difference between measured FWHM (full width at half maximum) and the unbroadened FWHM of single crystal which was taken to be 0.039° for both ZnO and ITO. With a measured FWHM of 0.40°, the estimated grain sized of ZnO film is about 23 nm.

3.2. Crystalline property of ITO

Fig. 2a,b show XRD curves of ITO films on ZnO-buffered glass and on bare glass respectively at a total pressure of 10 mTorr, oxygen ratio of 0.5%, and various substrate temperatures of 100, 200 and 300°C. It can be seen from Fig. 2 that, with the ZnO buffer applied, only (222) peaks of ITO and (0002) peaks of ZnO appear. The ITO films show single (222)-oriented highly-textured structures. The near-epitaxial growth of ITO on ZnO is possibly due to their small lattice mismatch between averaged neighboring oxygen–oxygen distance of bixbyite In_2O_3 to that of ZnO on the closest-packed planes. According to the Scherrer equation, with a FWHM of 0.182° for the 300°C deposited ITO film in Fig. 2a, the estimated grain size of ITO is about 57 nm ($\theta = 15.29°$ for (222) plane of ITO). It can be noted from Fig. 2 (see the noise fluctuation of the curve) that, with ZnO buffers, the XRD intensities of ITO films increase thousands of times compared to those films without ZnO buffer layers.

Fig. 3a,b show XRD curves of ITO films on ZnO-buffered glass and on bare glass respectively at a substrate temperature of 300°C, total pressure of 10 mTorr, and various oxygen ratios of 0, 0.5 and 3.3%. It can be seen that, without the ZnO buffer, ITO films favor (100) orientation at low oxygen content and (111) orientation at higher oxygen content. But when ZnO buffers are applied, the crystalline structure of ITO films changes drastically from mixed-oriented to highly single (111)-oriented.

3.3. Electrical property of ITO

The electrical property (resistivity) was examined to optimize the deposition process. A design of experiment was carried out by correlating the resistivity with deposition process in the process parameter spaces of oxygen ratio, total gas pressure, and substrate temperature. For reduced design complexity and size, the parameters were switched at the optimal points (lowest resistivity). For example, to find the optimal oxygen ratio, we fix the temperature and total gas pressure, and vary the oxygen ratio in the oxygen ratio parameter space. With one or two cycles of such a process, the optimal deposition conditions can be obtained. We will show the resistivity of ITO films in the parameter spaces of oxygen ratio, total gas pressure, and substrate temperature accordingly.

Fig. 4 shows the resistivity of ITO films on bare glass and ZnO-buffered glass as a function of oxygen ratio at a fixed substrate temperature of 300°C, and a fixed total pressure of 10 mTorr. From the figure it can be seen that the resistivity of ITO film on ZnO buffer shows remarkable decrease. For example, at an oxygen ratio of 0.5%, the resistivity of ITO film drops from 0.311 to 0.232 mΩ cm, which accounts for a 25% drop. This significant conductivity increase is believed

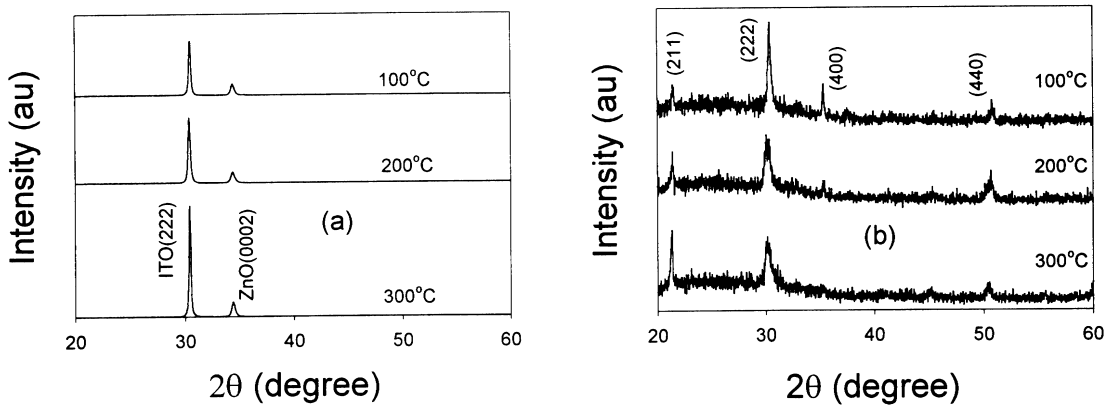

Fig. 2. XRD data of ITO films deposited on (a) ZnO/glass (left) and (b) glass (right), at various substrate temperature of 100, 200 and 300°C. The total gas pressure was 10 mTorr and the oxygen ratio was 0.5%.

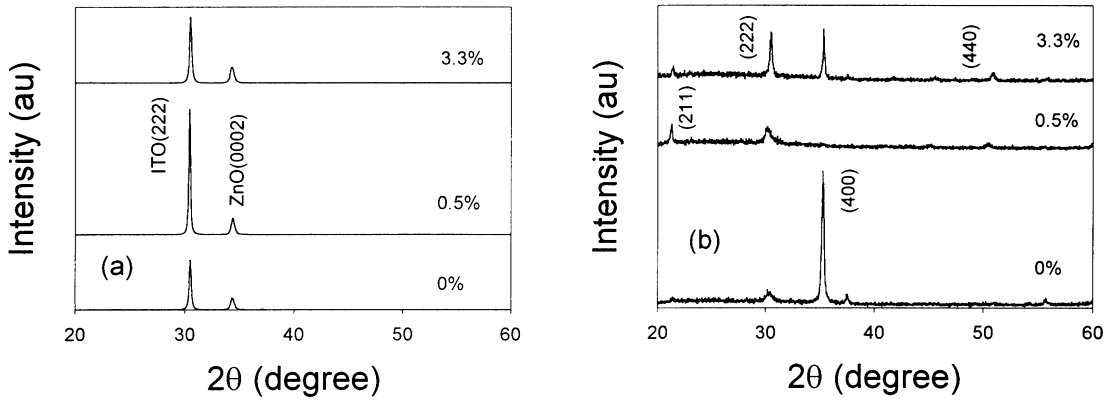

Fig. 3. XRD data of ITO films deposited on (a) ZnO/glass (left) and (b) glass (right), at various oxygen ratios of 0, 0.5, and 3.3%. The substrate temperature used was 300°C, the total gas pressure was 10 mTorr.

to be due to the better crystalline structure which results in an increase in the Sn solubility in In_2O_3 matrix and reduced grain boundary scattering.

From Fig. 4 it can also be seen that, with more deviation from optimal oxygen to argon ratio of 0.5%, the decrease of resistivity increases. From a process point of view, by applying a ZnO buffer, the process parameter space of oxygen ratio is increased. That is, there is a large tolerance to variation in process parameter–oxygen to argon ratio in sputtering.

Fig. 5 shows the resistivity of ITO films on bare glass and ZnO-buffered glass as a function of total gas pressure at a substrate temperature of 300°C, and an oxygen ratio of 0.5%. The optimal total pressure was found to be 15 mTorr. At the optimal total pressure of 15 mTorr, the resistivity of ITO film drops from 0.247 mΩ cm to 0.140 mΩ cm when the ZnO buffer is applied. These values are among the smallest values of ITO thin films reported [10].

Contrary to the resistivity in the oxygen ratio space, the resistivity in the pressure space has a maximum change at the optimal total gas pressure. So by applying ZnO buffer, the tolerance for total gas pressure becomes smaller. This means the pressure should be more precisely controlled compared to oxygen to argon ratio in the deposition process if ZnO/glass is used instead of glass.

The film deposition rate is a function of total gas pressure. Fig. 6 depicts ITO deposition rate as a function of total gas pressure with a substrate temperature fixed at 300°C and an oxygen ratio fixed at 0.5%. It is obvious from the Fig. 6 that the deposition rate decreases as the total gas pressure is increased.

Fig. 7 shows the resistivity of ITO films on bare glass and ZnO-buffered glass as a function of substrate temperature at a fixed total gas pressure of 15 mTorr, and oxygen ratio of 0.5%. The ZnO buffer was deposited at a substrate temperature of 300°C as mentioned before. It can be seen in the temperature parameter space, that the benefit of applying ZnO buffer disappears with more deviation from the optimal temperature (300°C in this experiment). High temperature clearly benefits the substrate choice of ZnO-buffered glass.

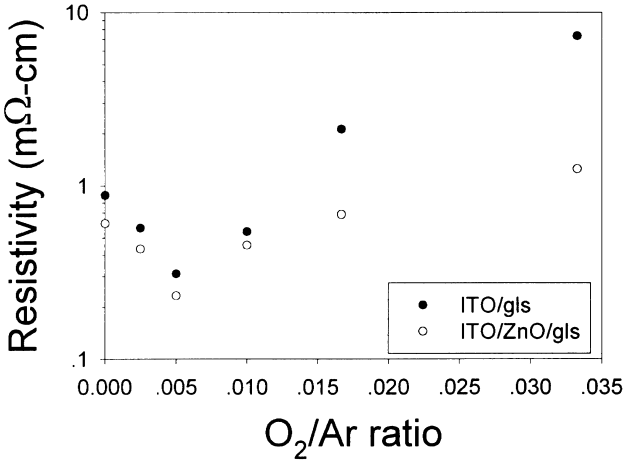

Fig. 4. Resistivity of ITO films grown on ZnO/glass and glass as a function of oxygen to argon ratio. The substrate temperature was 300°C, total gas pressure was 10 mTorr.

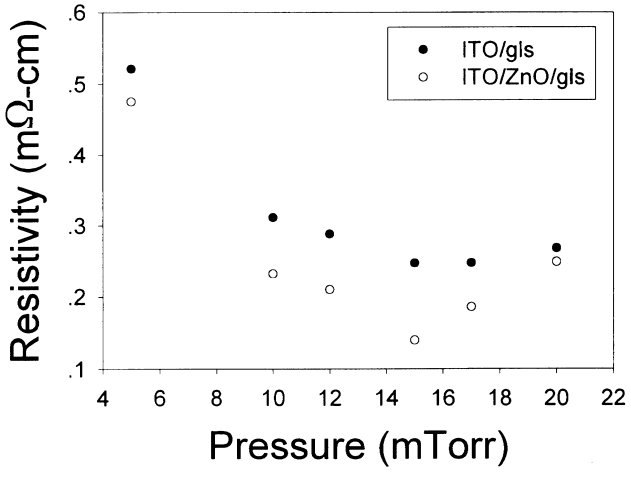

Fig. 5. Resistivity of ITO films grown on ZnO/glass and glass as a function of total gas pressure. The substrate temperature was 300°C, oxygen to argon ratio was 0.5%.

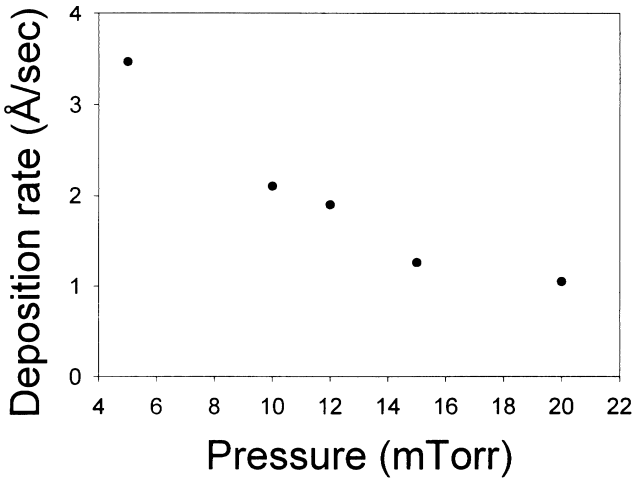

Fig. 6. Deposition rate of ITO films as a function of total gas pressure. The substrate temperature was 300°C, oxygen to argon ratio was 0.5%.

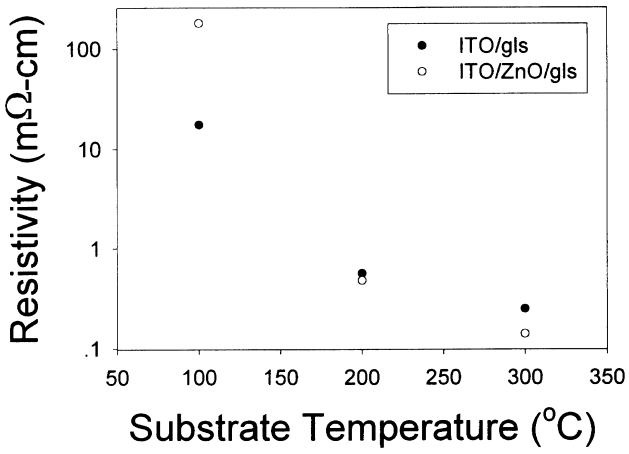

Fig. 7. Resistivity of ITO films grown on ZnO/glass and glass as a function of substrate temperature. The total gas pressure was 15 mTorr, oxygen to argon ratio was 0.5%.

Our result seems contradictory with those obtained by Yi et al. [7], who showed that the resistivity of ITO films grown on ZnO-buffered glass and glass by sputtering had comparable values. This divergence may be caused by the post-annealing in the forming gas after ITO sputtering. It was reported by Taga et al. that the resistivity of ITO films by evaporation was much smaller than that of ITO films by sputtering [5]. They believed that it is due to the ion bombardment during sputtering. The ion bombardment induced defects decrease either the carrier mobility or both of carrier concentration and mobility. They also showed that ITO films grown on crystalline substrates had a lower resistivity than ITO films on glass by e-beam evaporation (no ion bombardment). So more crystalline structure does have a positive effect on the resistivity of ITO films, provided that the fabrication process is free of ion bombardment.

In our experiment, a post-annealing of half an hour in the forming gas was performed to annihilate the defects induced by ion bombardment during sputtering. This is equivalent of fabricating ITO films by an ion-bombardment-free technique such as evaporation. The 50% decrease of resistivity at the optimal deposition condition is due to this forming gas annealing.

To illustrate our idea, room-temperature Hall effect measurements were performed for the samples deposited at the optimal process condition, i.e. 300°C substrate temperature, 0.5% oxygen ratio, 15 mTorr total gas pressure. The results are given in Table 2. ITO films with forming gas annealing and without forming gas annealing are both included.

From Table 2, it can be seen that with forming gas annealing, ITO on ZnO/glass has a relatively larger mobility and a slightly larger carrier concentration than ITO on bare glass. The remarkable mobility increase of ITO on ZnO-buffer glass comes from the drastic improvement of the crystal structure. The more crystalline structure means increased Sn solubility and less scattering centers. The slightly increased carrier concentration may come from the increased Sn solubility in In_2O_3 matrix.

For ITO films without forming gas annealing, it can be seen from Table 2 that the mobility, carrier concentration and resistivity are almost the same for ITO on glass and on ZnO-buffered glass. So the resistivity of sputtered ITO film is not sensitive to the crystallinity of ITO film itself. This is in good agreement with the result by Kamei et al. [4], who showed that the resistivity of heteroepitaxial grown ITO films on YSZ by sputtering had comparable values with that of ITO on glass. The insensitivity of resistivity on crystallinity is probably caused by ion bombardment in sputtering.

From Table 2, it can be inferred that the in situ forming gas annealing does have a positive effect on the resistivity of ITO film by sputtering. The effect is more obvious for crys-

Table 2
Electrical properties of ITO films on glass and ZnO/glass deposited at 300°C substrate temperature, 0.5% oxygen ratio, and 15 mTorr total gas pressure with and without forming gas annealing

		Resistivity ($\times 10^{-4}$ Ω cm)	Hall mobility (cm^2/V s)	Carrier density ($\times 10^{21}/cm^3$)
With forming gas annealing	Glass	2.47	22	1.15
	ZnO/glass	1.40	36	1.24
Without forming gas annealing	Glass	6.55	12	7.95
	ZnO/glass	6.40	15	6.51

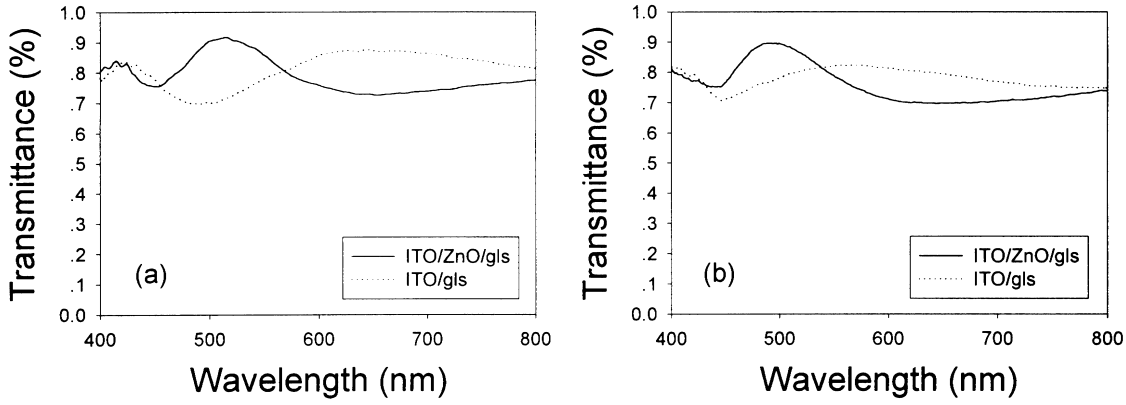

Fig. 8. Transmittance of ITO film grown on ZnO/glass (solid line) and glass (dashed line). The ITO films were grown at 300°C substrate temperature, 0.5% oxygen ratio, and two different total gas pressure of (a) 10 mTorr, (b) 15 mTorr.

talline ITO films. In situ forming gas annealing mainly annihilates the defects caused by ion bombardment inside ITO and results in a decrease of scattering centers and an increase of mobility. It also facilitates the activation of Sn in In_2O_3 matrix, which results in a higher carrier concentration. From the results that sputtered ITO films need and evaporated ITO films need not (shown by Taga et al. [5]) be annealed to decrease the resistivity, it is evident to argue that the presence of energetic particles in sputtering (ion bombardment) is the reason for the insensitivity of substrates (crystallinity of ITO). This is similar to the case of pulsed-laser deposited ITO films [11]. In pulsed laser deposition, there are also energetic particles present. These particles generate defects inside ITO films, which in turn make the resistivity of ITO insensitive to the substrates used.

The room-temperature Hall effect measurements were also performed for other samples deposited at 300°C substrate temperature and 0.5% oxygen ratio. The forming gas annealing effect is the same for all these samples. With forming gas annealing, ITO films became more substrate sensitive. All samples showed resistivity, carrier concentration and mobility improvements with ZnO buffers applied and forming gas annealing performed.

3.4. Optical property of ITO

The transmittance of the ITO films was characterized by a self-made visible spectrometer. The light source used was a tungsten lamp. The signal was collected by a CCD camera with a monochrometer (2 nm resolution). Fig. 8a shows the transmittance of ITO/ZnO/glass (solid line) and ITO/glass (dashed line) from 400 to 800 nm. These samples were grown under the condition of 300°C substrate temperature, 10 mTorr total pressure and 0.5% oxygen ratio. ITO films were about 2000 Å thick. In Fig. 8a, the overall transmittance is almost the same for ITO on ZnO/glass and ITO on glass. The increase of transmittance in the blue region and the lowering of transmittance the in red region for ITO on ZnO-buffered glass (compared to ITO on glass) is simply due to an etalon interference effect; this can be inferred by the changing of colors with different viewing angles.

Fig. 8b shows the transmittance of ITO films grown on ZnO/glass (solid line) and glass (dashed line) in the range of 400–800 nm. These samples were grown at 300°C substrate temperature, 15 mTorr total gas pressure and 0.5% oxygen ratio. The ITO film thickness was about 1200 Å. Fig. 8b shows a similar transmittance pattern to Fig. 8a.

4. Conclusion

In summary, we have performed an experiment designed to improve the crystal, electrical and optical properties of ITO thin films for display applications. By applying a thin layer of ZnO buffer, the ITO films showed a drastic increase in crystallinity. The conductivity of ITO films also showed remarkable improvement. The resistivity of the ITO film dropped nearly 50%. The transmittance kept almost the same for ITO films on glass and on ZnO-buffered glass. Effects of crystallinity and in situ forming gas annealing on ITO resistivity were also discussed. The sputtered ITO films with in situ forming gas annealing were similar to those evaporated ITO films in terms of electric properties.

Highly textured low-resistivity ITO films on ZnO-buffered glass may have potential applications in high-resolution flat-panel displays. They may also have applications wherever an ITO substrate with reduced resistivity and more crystalline structure is required. Since ZnO is also a transparent and conducting oxide, it is compatible with the ITO fabrication process. Hence it is practical to add one more ZnO process to the commercial ITO production line.

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