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Deposition of indium tin oxide films on polycarbonate substrates by radio-frequency magnetron sputtering

Wen-Fa Wu *, Bi-Shiou Chiou

Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu , Taiwan

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Abstract

Indium tin oxide (ITO) films have been deposited onto polycarbonate (PC) substrates by radio frequency (rf) magnetron sputtering. The influence of the oxygen content during sputtering on the film morphology, and the electrical and optical properties of the films have been investigated. Both the refractive index and the extinction coefficient decrease with increasing oxygen content. In this study, the figures of merit T^{10}/R_{sh} of the films are higher than those for low-temperature sputtered films reported in the literature. © 1997 Elsevier Science S.A.

Keywords: Coatings; Indium oxide; Optical properties; Sputtering

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1. Introduction

Transparent conductive indium tin oxide (ITO) films are used extensively in a variety of electronics and optoelectronics applications because of their high transmission in the visible range, high infrared reflection, and low electrical resistivity. The demand for ITO films with both low electrical resistivity and high transparency in the visible part of the solar spectrum has led to the development of various deposition techniques. Magnetron sputtering is considered to be one of the best methods for preparing high-quality ITO films. However, although ITO films with both high electrical conductivity and high visible transmittance have often been obtained, it is necessary to prepare them at high temperature (above 350 °C) during deposition or post-deposition annealing. Hence, in most of the work reported, ITO films were deposited onto various glass substrates that can withstand high-temperature annealing. Very few works have reported the deposition of ITO films at low-temperature on substrates such as plastics [1–4].

Transparent conductors on organic substrates have many applications, such as in plastic liquid crystal display devices, transparent electrostatic discharge and electromagnetic interference shielding materials, flexible electro-optical devices and unbreakable heat-reflecting mirrors [1,5]. Research is continuing in order to develop rf magnetron-sputtered ITO films on plastic substrates. In the previous work, ITO films were deposited onto acrylic substrates [1,2]. As the deformation temperature of acrylic is only 80 °C, a low substrate temperature and low rf power were maintained during sputtering to prevent acrylic deformation, and a low deposition rate (~ 14 Å min^{-1} at an rf power of 18 W) was obtained for film deposition [2].

In the present study, we employed polycarbonate as the substrate material. Polycarbonate has a higher deformation temperature (~ 140 °C) than acrylic [6] and the film deposition process can be carried out at a higher rf power, so that a higher deposition rate could be expected [7]. The effect of oxygen content in the sputtering atmosphere on the microstructure as well as the electrical and optical properties of the ITO films are investigated and discussed.

2. Experimental details

The ITO films were prepared by a commercial rf magnetron sputtering system (IonTech, UK). The sputtering target was a 1-inch diameter hot-pressed oxide ceramic (90 wt% In_2O_3 and 10 wt% SnO_2, 99.99% purity) supplied by Cerac, Inc., USA. The substrates employed were polycarbonate sheets ($4.6 \times 2.6 \times 1.3$ cm and $4.6 \times 2.6 \times 0.4$ cm), which were degreased ultrasonically in a dilute detergent solution, rinsed ultrasonically in deionized water, and blown dry in N_2 gas before they were introduced into the chamber. The sub-

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* Corresponding author.

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strate was fixed directly above the target with a target-to-substrate distance of 6 cm. A parallel experiment on ITO films deposited onto glass substrates was also carried out for comparison. The vacuum chamber was pumped by a diffusion pump. High-purity Ar and O_2 were introduced through a mass flow controller after the vacuum chamber was evacuated to about 2.66×10^{-4} Pa. The gas pressure was kept at 1 Pa and the sputtering power employed during deposition was 60 W.

The film thickness was measured with a stylus surface profiler. The sheet resistance of the samples was measured with a four-point probe and the resistivity of the film was calculated. An X-ray diffractometer was used to identify the crystalline phase of the films. A chemical binding energy analysis was performed using an X-ray photoemission spectroscope (XPS, Perkin PHI-590AM SAM/1905 ESCA, Massachusetts, USA) with an Mg Kα X-ray source. The microstructure of the films was analyzed using a scanning electron microscope (SEM, Hitachi S-4000, Japan) and a multimode scanning probe microscope (Digital Instruments, Inc., USA). The optical transmittance and reflectance of the films were measured with an ultraviolet–visible–near-infrared spectrophotometer (Hitachi U-3410, Japan) and a Fourier transform infrared (FTIR) spectrophotometer.

3. Results and discussion

The deposition rate, defined as film thickness divided by the deposition time, is important in controlling the film thickness, especially for optical coatings. In this study, a deposition rate of ~380 Å min^{-1} was obtained at an rf power of 60 W and an argon pressure of 1 Pa. X-ray diffraction patterns of the as-deposited ITO films indicate that the films have the cubic bixbyite structure of In_2O_3 [7–10]. Fig. 1 shows typical XPS survey spectra of the ITO films produced in this study. The elements In, Sn, O and C are found in the spectra.

The influence of the oxygen partial pressure on the microstructure of the film was investigated. Fig. 2 shows SEM micrographs of ITO films ~8000 Å thick deposited onto glass substrates at various oxygen percentages. As shown in Fig. 2, grainy surfaces can be observed for all specimens and the grain size tends to increase as the oxygen percentage increases. For the ITO films deposited at <1% oxygen, the ITO surface consists mostly of small grains. With further increases in oxygen content, the domain structure, as shown in Fig. 2(b,c), which is the gathering of small grains, is observed and the ITO films exhibit isolated domains ranging in size from ~80 to ~150 nm, embedded in the small grains on the surface. As shown in Fig. 2, the sizes and amounts of these domains increases with increasing oxygen percentage in the sputtering gas. Similar domain structures were also observed by Higuchi et al. [11].

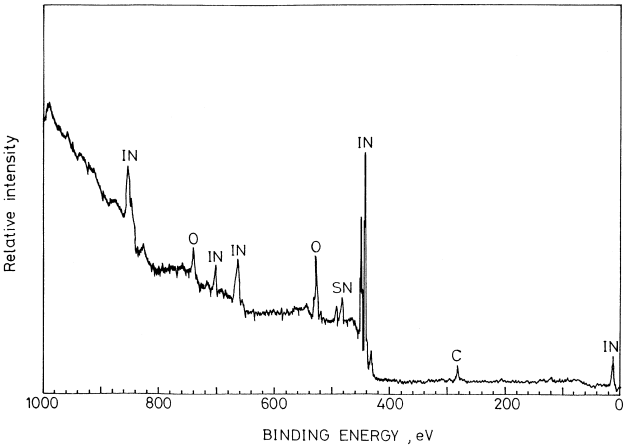

Fig. 1. Typical XPS survey spectrum of the ITO film deposited on a PC substrate.

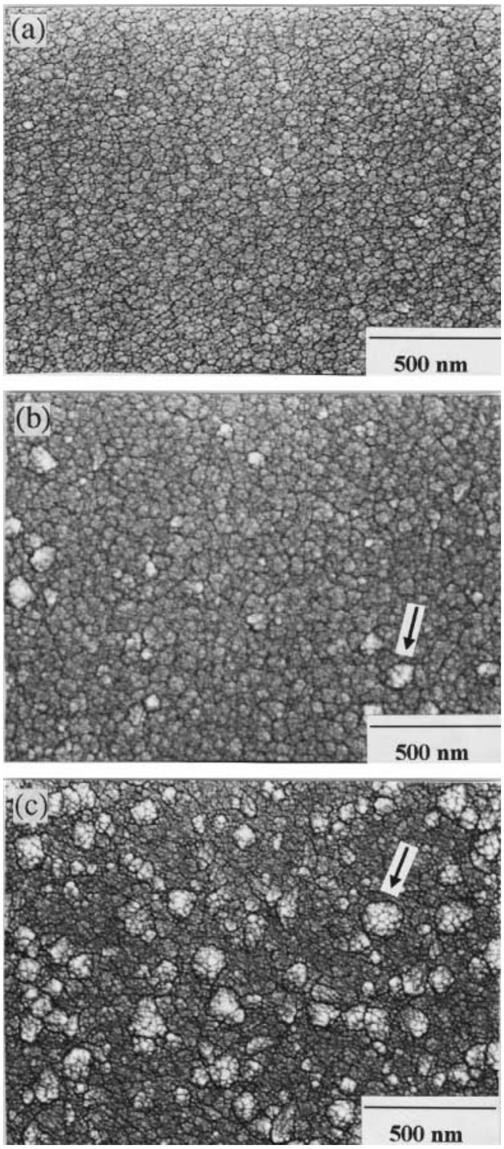

Fig. 2. SEM micrographs of ITO films ~8000 Å thick deposited on glass substrates at (a) 0%; (b) 1.5%; and (c) 3% oxygen. The arrows in (b) and (c) indicate the domain structure.

Fig. 3 shows cross sectional SEM micrographs of ITO films ~2000 Å thick prepared on glass at various oxygen

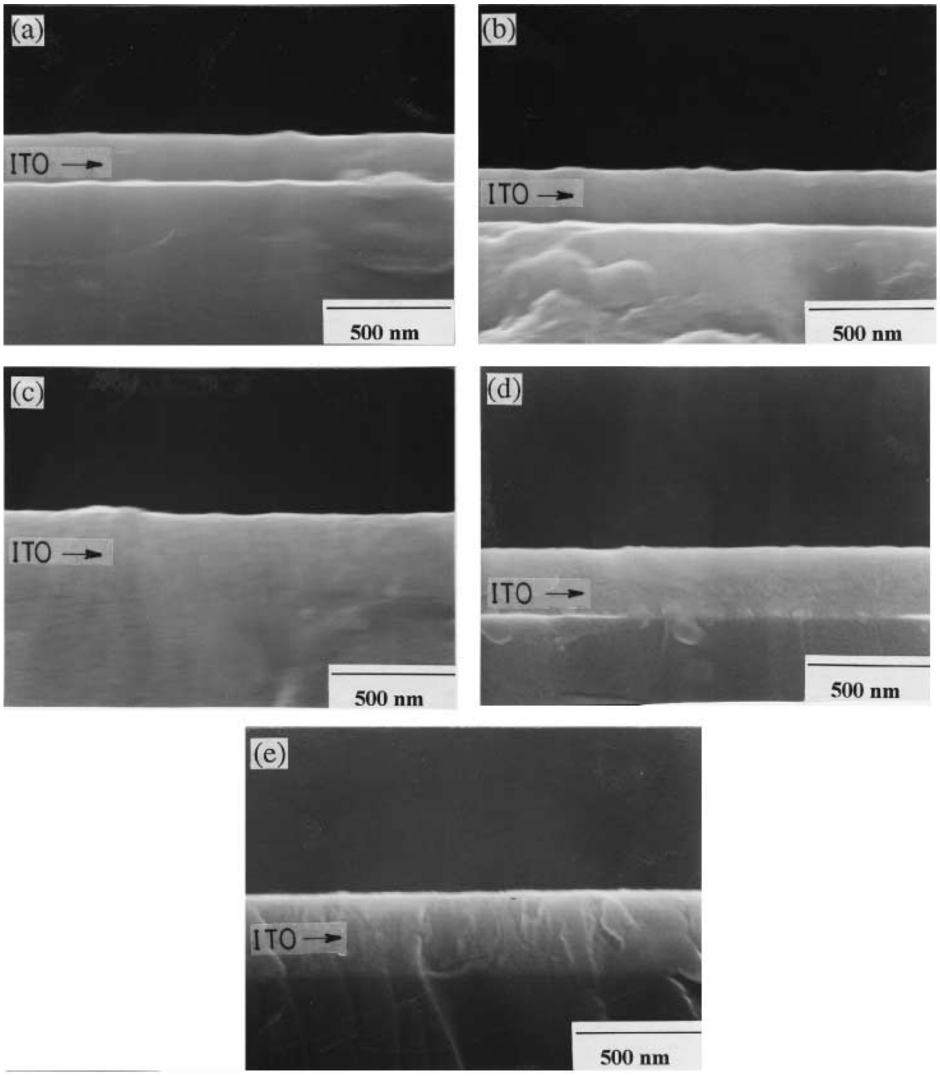

Fig. 3. Cross sectional SEM micrographs of ITO films prepared on glass substrates at (a) 0%; (b) 1.5%; (c) 2.8%; (d) 3.5%; and (e) 4.0% oxygen.

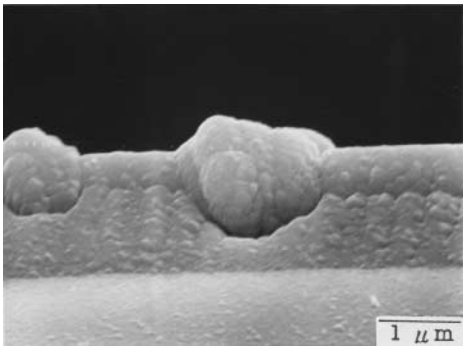

Fig. 4. Cross sectional SEM micrograph of the ITO film prepared on glass substrates with 2% oxygen. Film thickness: 15 000 Å.

percentages. A grainy structure appears and the typical columnar structure develops at an oxygen percentage $p > 2.8\%$, whereas columnar structures are not observed for $p \leq 2.8\%$. A particle-like structure is occasionally observed in the cross sectional SEM micrograph of the thick film (~15 000 Å) prepared at $p \geq 2\%$, as shown in Fig. 4. It is believed that film thickness affects the development of the particle-like structure. However, the detailed mechanism is not yet understood and remains to be determined.

Because the plastic substrate deforms during an electron microscopic investigation [2], atomic force microscope (AFM) was used to investigate the microstructure of films deposited on PC substrates. Fig. 5 shows AFM micrographs of the ITO films ~2000 Å thick prepared at various oxygen percentages. The size of the grainy columns increases from ~15 to ~20 nm as the oxygen percentage increases from 0% to 4.6%. This implies an improvement in the degree of crystallinity, and is in good agreement with results for films deposited on glass substrates [4,10].

Fig. 6 shows that the resistivity of the films increases with increasing oxygen percentage. It has also been found that the resistivity of ITO films deposited on PC substrates is higher than that of films deposited on glass substrates. Dobrowolski et al. [3], in their work on ITO films prepared by an ion-assisted evaporation process, reported that films deposited onto different substrates had different resistivities. The resistivity of ITO films deposited on Mylar substrates was higher

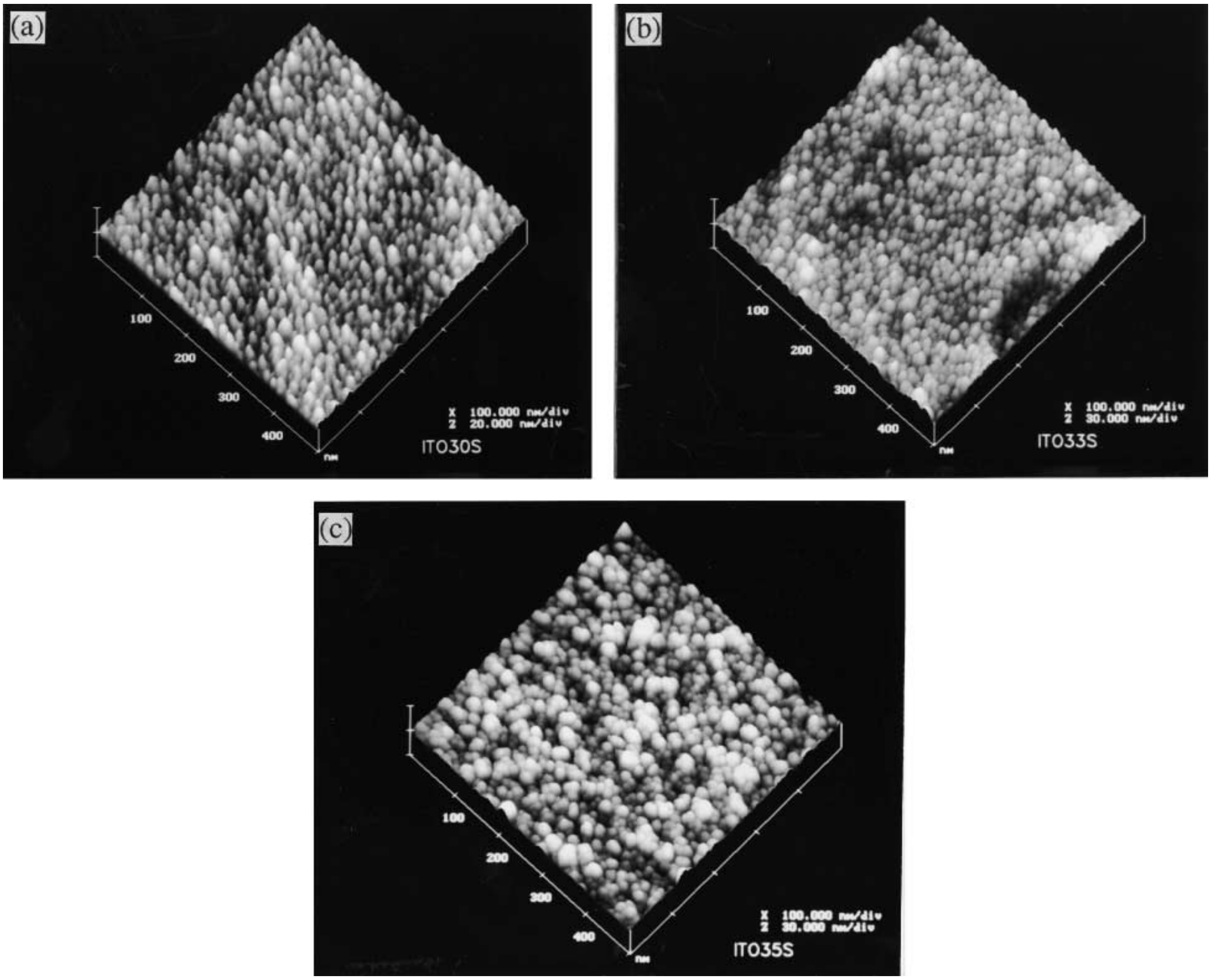

Fig. 5. AFM micrographs of ITO films prepared with (a) 0%; (b) 2.8%; (c) 4.6% oxygen.

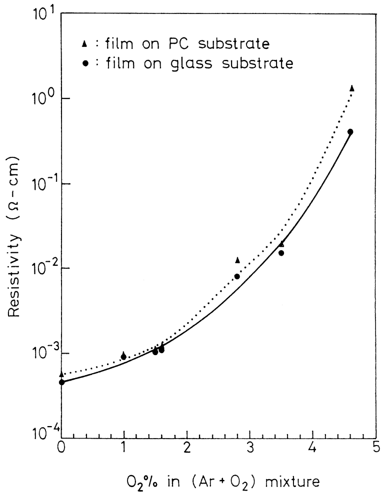

Fig. 6. Resistivity of ITO films as a function of oxygen percentage. Film thickness ~2500 Å.

than that of films on glass substrates. They suggested that this could be due to the high temperature attained by the glass substrates during evaporation. The residual thermal stress, S_T, of the as-deposited film is given by

$$S_T = E_f(a_f - a_s)(T_D - T), \quad (1)$$

where E_f is the Young's modulus for the film, a_f and a_s are average thermal expansion coefficients of the film and substrate, respectively, T_D is the film deposition temperature and T is the temperature after deposition. The thermal expansion coefficients of In_2O_3, Corning 7059 glass, and PC are 7.2×10^{-6} [12], 4.6×10^{-6} and 39×10^{-6} °C^{-1} [6], respectively, so that larger thermal stresses would develop when PC substrates are employed than those when glass substrates are employed. The difference in the residual thermal stress could be one reason for the differences in film resistivity shown in Fig. 6.

Increases in resistivity with increasing oxygen pressure have also been reported by other researchers [13,14]. A parallel experiment on ITO films deposited on glass substrates revealed that the carrier concentration decreases from $\sim 2.3\times10^{22}$ to 1.3×10^{19} cm^{-3} as the percentage of oxygen in the sputtering gas increases from 0 to 4.5% [4,10], while the carrier mobility ranges from 11 to 21 cm^2 V-s^{-1} in the oxygen percentage range of interest [4,10]. The incorporation of oxygen leads to a decrease in oxygen vacancies in the films, and hence to a fall in the charge carrier concentration, as follows:

$$\tfrac{1}{2}O_{2(g)} + V_O^- + 2e' \rightarrow O_O. \quad (2)$$

The high resistivity at high oxygen percentages is therefore attributed to the low charge carrier concentration of the film.

Fig. 7 shows the spectral characteristics of polycarbonate and glass substrates. An average transmittance of ~92% is obtained for Corning 7059 glass, but strong absorption is observed for PC substrates regardless of thickness. Hence, as the transmittance of films deposited on PC substrates is measured, a bare PC substrate of the same thickness is used as a reference to eliminate the effects of strong absorption for PC substrates. The absorption observed at ~1400 nm and ~1900 nm is caused by adsorbed water vapor [15]. A discontinuity of 1–2% is observed when the measuring wavelength range is switched from the visible to the near-infrared (850 nm), as the detector of the spectrophotometer is switched from a photomultiplier to a PbS cell [15].

Fig. 8 shows the transmittance of the as-deposited films prepared at various oxygen percentages. The transmittance of films prepared at 2% and 3% O_2 are higher than those of films prepared at $\leq 1\%$ O_2. It is believed that the oxygen deficiency in the ITO films prepared at low oxygen percentages contributes to the blackening of the ITO films [7,8,10].

The refractive index and extinction coefficient of the ITO films were calculated on the basis of Swanepoel's method [8,16]. Fig. 9 shows the refractive indices and extinction coefficients versus wavelength for ITO films deposited at various oxygen percentages. As indicated in Fig. 9(a), the refractive indices of the ITO films decrease with increasing oxygen pressure. This decrease suggests that the average density of the film deposited at high oxygen pressure is less than that deposited at low oxygen pressure. This indicates that there are internal voids and surface irregularities in the film deposited at high oxygen pressures. These observations and previous SEM observations are in good agreement (see Fig. 2). Since the transmittance of the film is enhanced with

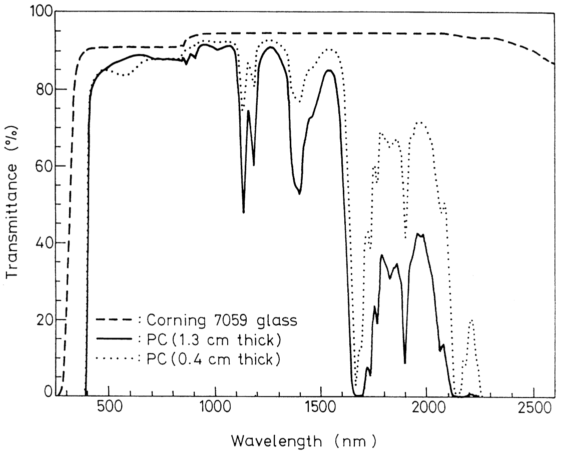

Fig. 7. Spectral characteristics of polycarbonate and glass substrates.

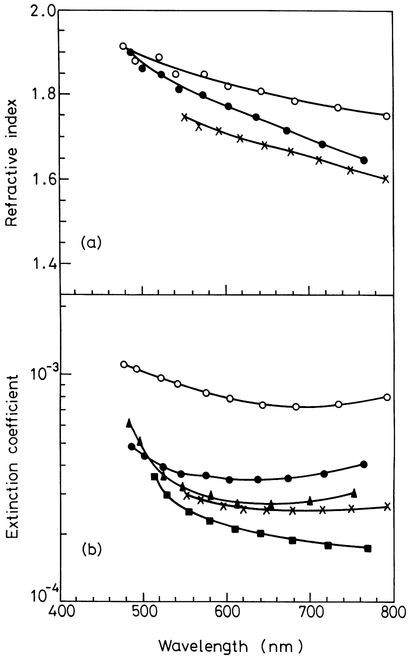

Fig. 9. (a) Refractive indices and (b) extinction coefficients versus wavelength for as-deposited ITO films prepared with various oxygen percentages. Film thickness ~1.1 μm.

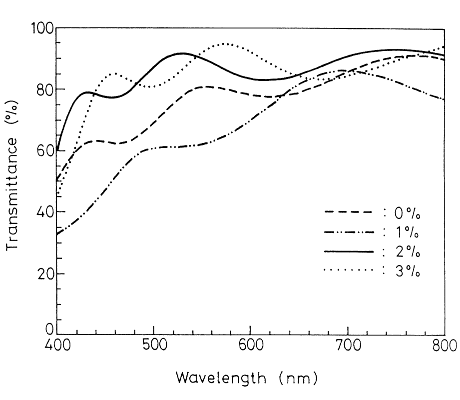

Fig. 8. Transmittance of ITO films prepared on PC substrates with various oxygen percentages. Film thickness ~2000 Å.

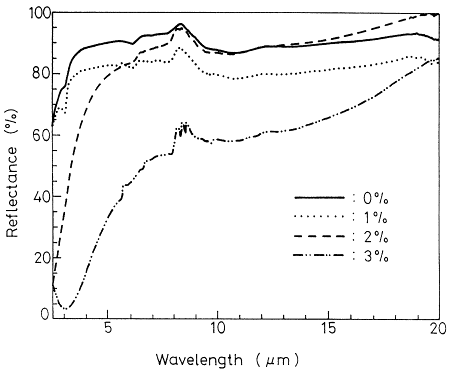

Fig. 10. Infrared reflectance as a function of wavelength for films deposited on PC substrates with various oxygen percentages. Film thickness ~2000 Å.

Table 1
Comparison of low-temperature sputtered indium tin oxide films prepared by different researchers

Reference	Substrate	Substrate temperature (°C)	Sheet resistance, R_{sh} (Ω/square)	Transmittance (%) ($\lambda = 5500$ Å)	Figure of merit ($\times 10^{-3}\ \Omega^{-1}$)	
					T^{10}/R_{sh} [c]	T/R_{sh}
Chiou and Hsieh [1]	Acrylic	50	19.06	74	2.58	38.6
Karasawa and Miyata [18]	Glass	Near room temperature	55	84	3.18	15.2
Mukherjee [a] [19]	Acrylic, glass, polycarbonate	–	20	81	6.08	40.5
Davis [20]	Glass, quartz	30	300	70	0.09	2.33
Present work [b]	Polycarbonate	<50	27.3	90	12.7	32.9

[a] Did not specify the type of the substrate.
[b] Film prepared with 2% oxygen.
[c] T^{10}/R_{sh} is the tenth power of T divided by R_{sh}.

increasing oxygen pressure, the ITO films deposited at high oxygen pressure have smaller extinction coefficients, as indicated in Fig. 9(b).

Fig. 10 shows the IR reflectance as a function of wavelength for films deposited at various oxygen percentages. The IR reflectance of the ITO films decreases significantly at high oxygen percentage. Frank et al. [17] showed that the IR reflectance R can be expressed by

$$R = 1 - \frac{4\epsilon_0 c_0}{e}\frac{1}{Nd\mu}, \qquad (3)$$

where c_0 is the velocity of light, ϵ_0 is the permittivity of free space, e is the electronic charge, N is the carrier concentration, d is the film thickness, and μ is the mobility of the free carriers. According to Eq. (3), the IR reflectance increases with the product of the carrier concentration N and carrier mobility μ. As discussed previously, the films deposited at high oxygen percentages have higher resistivities and smaller values of the product $N\mu$ than those deposited at low oxygen percentages. Hence, the IR reflectance of the film decreases with increasing oxygen percentage, as observed.

For transparent conductor applications, it is essential to optimize the electrical and optical coating parameters. The figure of merit, which can be defined in several ways, is used to judge the performance of transparent conducting films. In Table 1, two common definitions of the figure of merit are adopted. The figures of merit T/R_{sh} of the ITO films deposited on polycarbonate substrates are comparable with those deposited on acrylic and glass substrates. In this study, the values of T^{10}/R_{sh} for the ITO films are higher than those for low-temperature sputtered films reported in the literature.

4. Conclusions

1. ITO films were deposited on polycarbonate substrates by rf magnetron sputtering. The X-ray diffraction patterns indicate that the as-deposited film has cubic bixbyite structure of In_2O_3.

2. The grain sizes of the films increase as the oxygen content in the sputtering ambient increases. The addition of oxygen improves the crystallization of the film. The results of AFM investigations indicate that the size of grainy column of the film increases from ~15 to ~20 nm as the percentage of oxygen increases from 0 to 4.6%.

3. The resistivities of the films range between $\sim 6 \times 10^{-4}$ and ~2 Ω-cm as the oxygen content is increased from 0 to 4.6%. The high resistivity at high oxygen percentage is attributed to the low charge carrier concentration of the film.

4. Both the refractive index and the extinction coefficient of the film decreases as oxygen percentage increases. In addition, the lower charge carrier concentration of the films prepared at higher oxygen percentage results in a decrease in the IR reflectance of the film.

5. The figures of merit T^{10}/R_{sh} for the ITO films deposited on polycarbonate substrates are higher than those for low-temperature sputtered films reported in the literature.

Acknowledgements

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References

[1] B.S. Chiou and S.T. Hsieh, *Thin Solid Films*, *229* (1993) 146.
[2] B.S. Chiou, S.T. Hsieh and W.F. Wu, *J. Am. Ceram. Soc.*, *77* (1994) 1740.
[3] J.A. Dobrowolski, F.C. Ho, D. Menagh, R. Simpson and A. Waldorf, *Appl. Opt.*, *26* (1987) 5204.
[4] W.F. Wu, *Rf Magnetron Sputtered ITO Films and ITO Films with Antireflective and Hard Coating*, Ph.D. Thesis, National Chiao Tung University, Hsinchu, June 1994.
[5] J.M. Margolis, *Conductive Polymers and Plastics*, Chapman & Hall, London, 1989.

[6] D. Grzegorczyk and G. Feineman, *Handbook of Plastics in Electronics*, Reston, Virginia, 1974.
[7] W.F. Wu and B.S. Chiou, *Thin Solid Films*, *247* (1994) 201.
[8] W.F. Wu and B.S. Chiou, *Semicond. Sci. Technol.*, *9* (1994) 1242.
[9] W.F. Wu and B.S. Chiou, *Appl. Surf. Sci.*, *68* (1993) 497.
[10] W.F. Wu and B.S. Chiou, *Semicond. Sci. Technol.*, *11* (1996) 196.
[11] M. Higuchi, M. Sawada and Y. Kuronuma, *J. Electrochem. Soc.*, *140* (1993) 1773.
[12] Y. Shigesato, S. Takaki and T. Haranou, *Appl. Surf. Sci.*, *48/49* (1991) 269.
[13] K. Ichihara, N. Inoue and M. Okubo, *Thin Solid Films*, *245* (1994) 152.
[14] S. Honda, A. Tsujimoto, M. Watamori and K. Oura, *Jpn. J. Appl. Phys.*, *33* (1994) L1257.
[15] Instruction manual for Hitachi Model U-3410 recording spectrophotometer.
[16] R. Swanepoel, *J. Phys. E: Sci. Instrum.*, *16* (1983) 1214.
[17] G. Frank, E. Kauer and H. Köstlin, *Thin Solid Films*, *77* (1981) 107.
[18] T. Karasawa and Y. Miyata, *Thin Solid Films*, *223* (1993) 135.
[19] A. Mukherjee, *Vacuum*, *39* (1989) 537.
[20] L. Davis, *Thin Solid Films*, *236* (1993) 1.