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Antireflective coating for ITO films deposited on glass substrate

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The refractive index *n* of radio-frequency (r.f.) magnetron sputtered indium tin oxide (ITO) films varies with sputtering parameters, such as sputtering power and oxygen percentage in the sputtering ambient. In this study, the feasibility to fabricate multilayer antireflective (AR) coating with a single ITO target by controlling the sputtering conditions is explored. Reduction in the reflectance can be achieved by using a one-quarter-wavelength inner layer ITO with a refractive index $n = 1.87$ and a one-quarter-wavelength outer layer ITO with $n = 2.17$. Hence, a single ITO target suffices in the preparation of multilayer AR coating. This simplifies the deposition processes and equipment for the fabrication of AR coating. Surface corrugation, another approach to the reduction of reflectance, is also discussed.

1. Introduction

Indium tin oxide (ITO) is an In_2O_3 based material that has been doped with Sn to improve electrical conductivity. Tin acts as a cationic dopant in the In_2O_3 lattice and substitutes on the indium sites to bind with interstitial oxygen. The presence of SnO_2 would result in n doping of the lattice because the dopant would add electrons to the conduction band [1]. The ITO film, with a band gap of approximately 3.8 eV, is highly transmissive in the visible region [2]. Hence, transparent conductive ITO film has many applications, such as in transparent electrodes, anti-reflection coatings, display devices, and photoelectronic devices [3–5]. In the design of anti-reflection (AR) coatings, materials with low refractive indices such as SiO_2 ($n = 1.46$) and MgF_2 ($n = 1.38$) are used as coating for ITO films to reduce unwanted reflections at the surface of the optical elements [6–8]. However, because MgF_2 and SiO_2 are electrical insulators this exhibits a limitation of ITO film in the application of display devices due to the high resistivity of the SiO_2 (or MgF_2) coating. In addition, multiple source materials are required in the preparation of multi-layer AR coatings, this complicates the deposition processes and equipments for the fabrication of AR coating.

Previous studies reveal that the electro-optical properties of radio frequency (r.f.) sputtered ITO films are sensitive to sputtering parameters, such as r.f. power [9–11], oxygen content in the sputtering ambient [1], substrate roughness [12], and annealing conditions [13]. It is anticipated that the refractive index of the ITO films can be varied by changing the sputtering parameters during deposition of ITO. Hence, the objective of this research is to explore the feasibility of the multilayer antireflective coating design with ITO films of various refractive indices obtained by varying the sputtering conditions.

2. Experimental procedures

ITO films were prepared by using a commercial r.f. magnetron sputtering system (Ion Tech, UK). The sputtering target was a 1 inch 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 Corning 7059 glass, 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 substrate holder was fixed directly above the target and was rotated at ~ 10 r.p.m. by a motor. The target-to-substrate distance was 5 cm and a mechanical shutter was attached to the target.

The vacuum chamber was a stainless steel bell jar pumped by a conventional oil diffusion pump (Diffstak 250, Edwards, UK). High-purity Ar (99.999%) and O_2 (99.5%) were introduced through a mass flow controller after the vacuum chamber was evacuated to about 3.1×10^{-4} Pa. The gas pressure was monitored with a precision ionization gauge and was kept at 1 ± 0.03 Pa during deposition. The r.f. power (13.56 MHz) was introduced through an r.f. power supply (RF Plasma Products, Inc., USA) with an automatic matching network which could be tuned for minimum reflected power. Before deposition, the target was presputtered to remove any contaminants and eliminate any differential sputtering effects. The presputtering time was 20 min for pure Ar and was increased to 30 min as O_2 was added to the sputtering ambient.

The film thickness was measured with a stylus surface profiler. The optical transmittance of the films was measured with an ultraviolet-visible-near infrared spectrophotometer (Hitachi U-3410, Japan).

3. Results and discussion

The refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ of the ITO film are calculated from transmission spectrum of the film. According to Swanepoel's method [14], which is based on the idea of Manifacier *et al.* [15] of creating the envelopes of interference maxima and minima in the transmission spectra, an approximate initial value of the refractive index of the film n_0 in the spectral region of medium and weak absorption, can be calculated by the expression

$$n_0 = \left[N + (N^2 - s^2)^{1/2}\right]^{1/2} \tag{1}$$

where

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \tag{2}$$

here T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength λ, one being measured and the other calculated; s is the refractive index of the Corning 7059 glass substrate and a value of 1.53 is used. The basic equation for interference fringes is

$$4nd = m\lambda \tag{3}$$

where m is an even integer for maxima and an odd integer for minima, and d is the film thickness measured with a stylus surface profiler. The order of a given extremum m_0 can be estimated from Equation 3 using d and the corresponding n_0. In addition, the values of m_0 can be determined by a simple graphical method based on Equation 3. This expression can be rewritten for that purpose as

$$\ell = 4d\left(\frac{n_0}{\lambda}\right) - m_1 \tag{4}$$

where $\ell = 0, 1, 2, \ldots$ and m_1 is the first extremum. Therefore, plotting l against n_0/λ yields a straight line with slope $4d$ and intercept on the y axis of $-m_1$. From this plot the values of m_1 and hence each corresponding order of a given extremum m_0 can be estimated. The orders of m of the neighboring extrema are in fact consecutive integers, even for the maxima and odd for the minima of the transmission. The final value of n for each extremum is obtained by substituting film thickness d and the corresponding exact integer values of m associated with each extreme point in Equation 3. The value of the extinction coefficient k is obtained by the following equations

$$E_M = \frac{8n^2 s}{T_M} + (n^2 - 1)(n^2 - s^2) \tag{5}$$

$$x = \frac{E_M - \left[E_M^2 - (n^2 - 1)^3(n^2 - s^4)\right]^{1/2}}{(n - 1)^3(n - s^2)} \tag{6}$$

$$x = \exp\left(-\frac{4\pi k}{\lambda}d\right) \tag{7}$$

The refractive index and extinction coefficient as functions of wavelength for the ITO films deposited at different sputtering powers are shown in Fig. 1. The refractive index of the ITO film decreases with the wavelength λ, i.e. $dn/d\lambda < 0$. This is consistent with what one would expect from a Kramers–Kronig analysis [16]. It is seen that the ITO films deposited at high sputtering power have large values of refractive index and extinction coefficient. The n value at 550 nm ranges between 1.97 (20 W) and 2.17 (100 W). Fig. 2 gives the refractive index and extinction coefficient versus

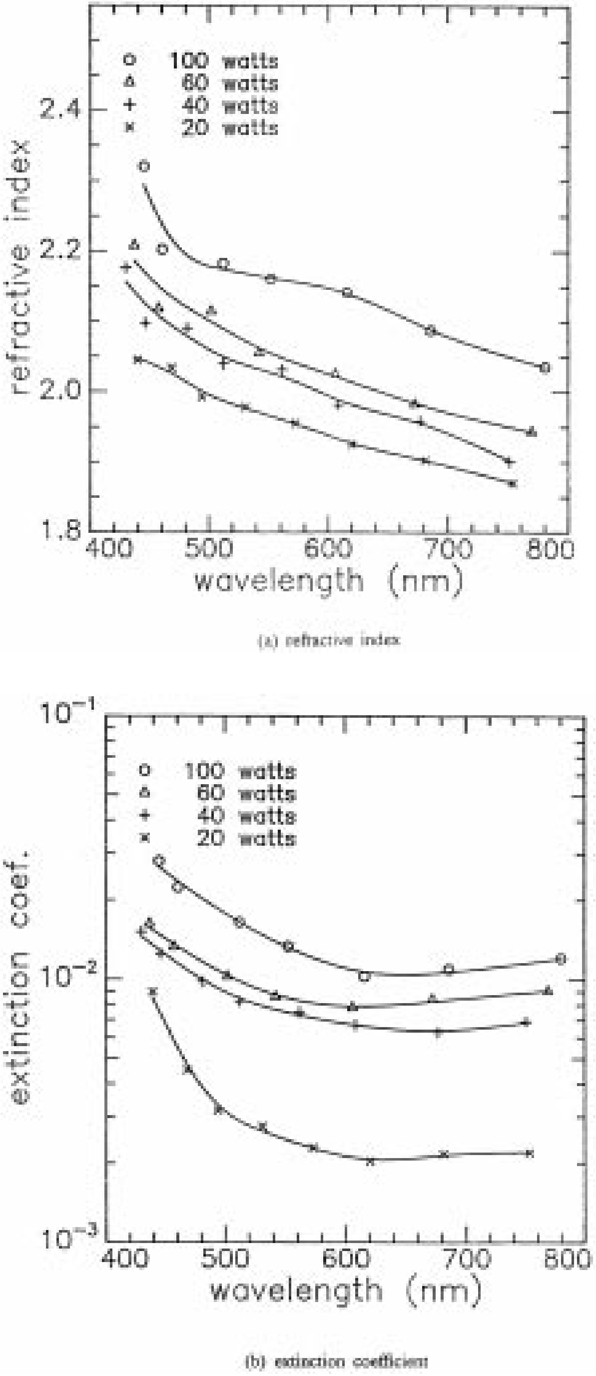

Figure 1 (a) Refractive index and (b) extinction coefficient versus wavelength for the as-deposited ITO films prepared at various sputtering power, film thickness 600 nm, sputtering ambient 0% oxygen.

wavelength for films prepared under various oxygen percentage. At 20 W, decreases in n and k are observed when the oxygen content increased from 0% to 2%. However, no apparent difference is found in k between samples prepared under 2% O_2 and those under 8% O_2. The n value at 550 nm ranges from 1.97 (0% O_2) to 1.87 (8% O_2).

When a light wave is incident on a system of thin films consisting of an assembly of l layers ($j = 1$ to l, with $j = 1$ as the outermost layer) on a substrate of refractive index n_S, the characteristic matrix of the optical system can be given by [17]:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{ \prod_{j=1}^{l} \begin{bmatrix} \cos\delta_j & i\sin\delta_j/\eta_j \\ i\eta_j\sin\delta_j & \cos\delta_j \end{bmatrix} \right\} \begin{bmatrix} 1 \\ \eta_s \end{bmatrix} \quad (8)$$

where

$$\delta_j = (2\pi/\lambda)(N_j t_j \cos\theta_j) \quad (9)$$

is the effective phase thickness of the jth layer; λ is the wavelength of the incident radiation in vacuo, and θ_j is the angle of refraction in the jth layer and is related to the angle of incidence θ by Snell's law:

$$N_0 \sin\theta = N_j \sin\theta_j \quad (10)$$

$N_j t_j$ and $N_j t_j \cos\theta_j$ are called the optical thickness and the effective optical thickness, respectively.

The equivalent optical admittance Y, the reflectance R, transmittance T and absorption A of the system can be given by

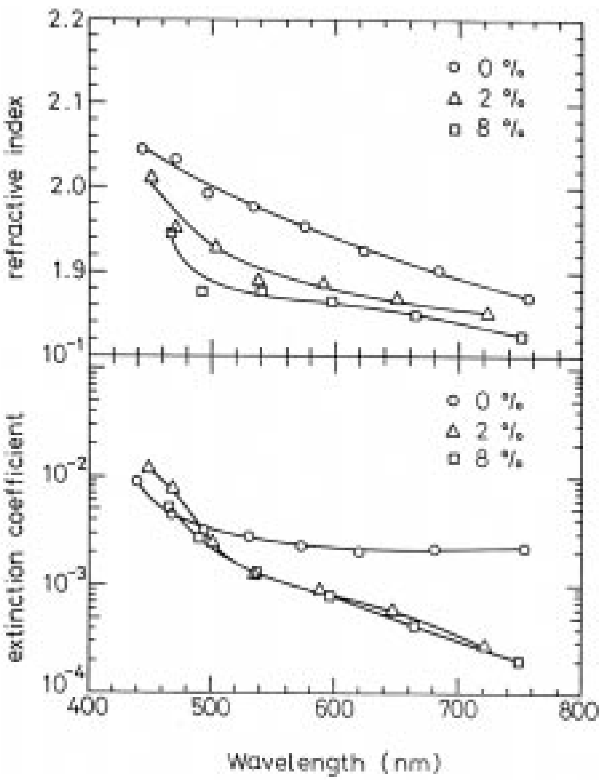

Figure 2 (a) Refractive index and (b) extinction coefficient versus wavelength for the as-deposited ITO films prepared under various oxygen percentages. film thickness 720 nm, sputtering power 20 W.

$$Y = C/B \quad (11)$$

$$R = \left(\frac{n_0 - Y}{n_0 + Y}\right)^2 \quad (12)$$

$$T = \frac{R_e n_0 (1 - R)}{R_e (BC^*)} \quad (13)$$

$$A = 1 - R - T \quad (14)$$

where C^* is the complex of C element, n_0 is the refractive index of incident medium ($n_0 = 1$ for air) and R_e is the real part of R.

On the basis of Equations 8 to 12, when the optical thickness of a single-layer coating is adjusted so that $n_1 d_1 = \lambda/4$, zero reflectance occurs if $n_1 = \sqrt{n_0 n_s}$. However, the substrate employed in this study has an n_S of 1.53 which suggests an n_1 (1.24) much smaller than those of ITO films. The reflectance of a $\lambda/4$ ITO coating as a function of wavelength is shown in Fig. 3. The R values increases with the increase of sputtering power and, hence, the refractive index.

When the thickness of a single layer coating is adjusted so that $n_1 d_1 = \lambda/2$, the reflectance can be reduced to

$$R = \left(\frac{n_0 - n_s}{n_0 + n_s}\right)^2 \quad (15)$$

which is equivalent to an uncoated substrate at a wavelength λ, as shown in Fig. 4 for $\lambda = 550$ nm. However, the reflection is appreciable and, due to the absorption of the coating, the transmittances are larger than those of a bare substrate.

According to Equations 8 to 12, the reflectance of a non-absorbing double-layer ($\lambda/4 - \lambda/4$) coating can be expressed as;

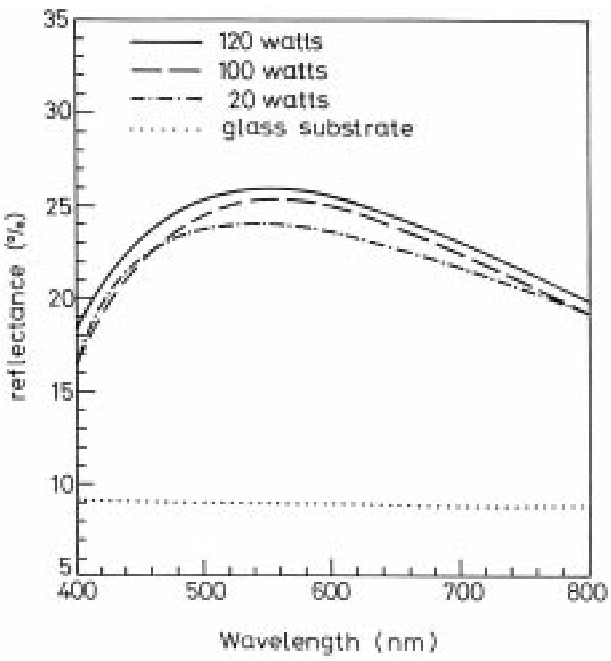

Figure 3 Reflection spectra of $\lambda/4$ ITO coating prepared at various sputtering powers; $\lambda = 550$ nm.

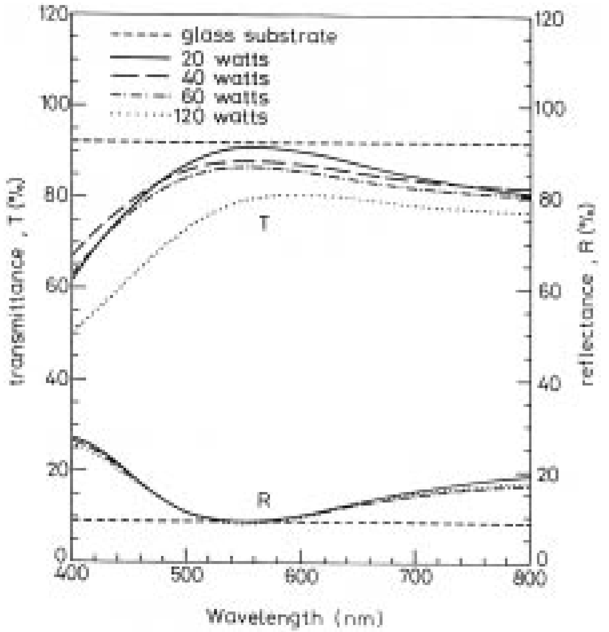

Figure 4 The transmission and reflection spectra of λ/2 ITO coating prepared at various sputtering powers; $\lambda = 550\,\text{nm}$.

$$R = \left(\frac{n_0 n_2^2 - n_1^2 n_s}{n_2 n_2^2 + n_1^2 n_s}\right)^2 \tag{16}$$

A zero reflectance requires:

$$\frac{n_1}{n_2} = \sqrt{\frac{n_0}{n_s}} = 0.808 \tag{17}$$

thus, the refractive index of the inner layer (n_2) should be larger than that of the outer layer (n_1). The n values of films in this study range from 1.97 to 2.17. Setting n_2 equal to 2.17, one finds that R decreases with n_1, as obtained from Equation 16 and shown in Fig. 5. The reflection spectra of three double-layer $(\lambda/4 - \lambda/4)$ coatings prepared under various conditions and one single layer $(\lambda/2)$ coating are exhibited in Fig. 6. The minimum reflectances are 7.45%, 6.46%, and 5.71% for samples $\lambda/4\,(40\,\text{W})^*$ $- \lambda/4\,(100\,\text{W})$, $\lambda/4\,(20\,\text{W}) - \lambda/4\,(100\,\text{W})$, and $\lambda/4\,(20\,\text{W}, 8\%\text{O}_2)^\dagger - \lambda/4\,(100\,\text{W})$, respectively. The n values for the inner layers $\lambda/4\,(40\,\text{W})$, $\lambda/4\,(20\,\text{W})$, and $\lambda/4\,(20\,\text{W},\ 8\%\ \text{O}_2)$ are

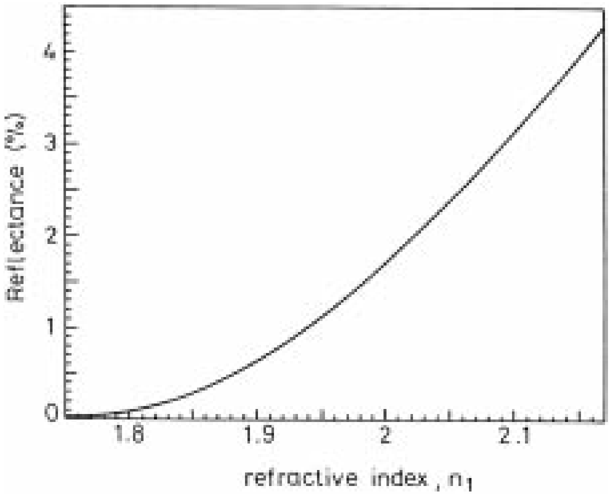

Figure 5 Calculated reflectance as a function of outer layer refractive index (n) for a two layer AR coating. The n of the inner layer is 2.17.

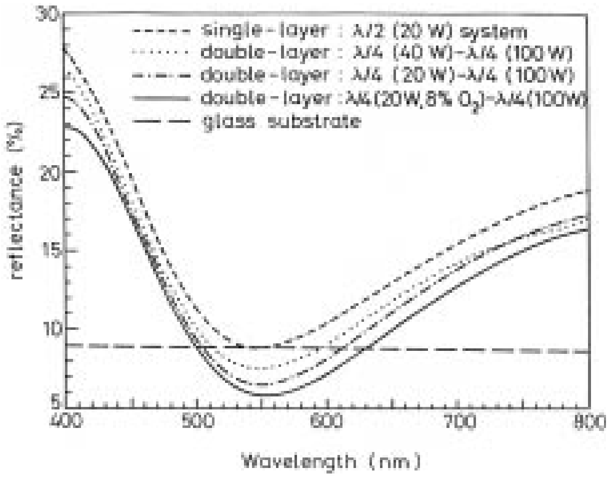

Figure 6 Reflection spectra of four coating systems. Note (20 W, 8%) means films sputtered at 20 W with 8% O_2.

2.03,1.97, and 1.87, respectively. The R does decrease with the increase of n_1, as suggested in Fig. 5. It is also noted that the double layer ITO coatings $(\lambda/4 - \lambda/4)$ have lower reflectance than the single layer $(\lambda/2)$ one. Hence, it is feasible to design multilayer AR coatings with a single ITO target by adjusting the sputtering parameters, such as oxygen concentration in the sputtering ambient and sputtering power. The presence of oxygen during sputtering enhances the crystallization of the film and increases the film grain size. The addition of oxygen reduces the oxygen-deficient region of the film and, consequently, the optical transmittance of the film is improved while the film conductivity decreases [1]. The structure and orientation of ITO films also strongly depends on the energy of the sputtered particles arriving at the substrate. The preferred orientation of the ITO films changes from (2 2 2) to (4 0 0) as the sputtering power increases. A high sputtering power causes the increase of oxygen vacancies in the films and results in the loss of optical transmittance of the films [9–11]. Hence, scrupulous care is needed in the design of multilayer AR coatings.

The n_1 and n_2 for a $\lambda/4\,(20\,\text{W}, 8\%\text{O}_2) - \lambda/4\,(100\,\text{W})$ coating at 550 nm are 1.87 and 2.17, respectively. The reflectance of the coating is $\sim 0.41\%$. The backside reflectance of the substrate is $\sim 4.20\%$. These add up to a total reflectance of $\sim 4.61\%$, as compared to 5.71% of the measured datum. The discrepancy between the experimental data and calculated data may be due to factors such as accuracy in thickness measurement, statistical deviation of the refractive index, and absorption of the film materials.

An alternative approach to single layer AR coating is to employ a high spatial-frequency rectangular-groove surface structure that behaves optically as an antireflection coating. Enger and Case [18] reported a significant reduction in R by etching linear fringe patterns on quartz. Motamedi *et al.* [19] generated pillar arrays on silicon substrate to simulate a single homogeneous AR layer Theoretical derivations by Gaylord *et al.* [20] demon-

*Film sputtered at 40 W, pure Ar.
†Film sputtered at 20 W, 8% O_2.

strated that zero reflectivity can be achieved by employing high-frequency rectangular grooves. However, the dimensions of the grooves are around one to one-tenth of the wavelength, which are too small to be etched precisely in the case of ITO [21]. Nonetheless, a preliminary attempt was made by fabricating an ITO coating with an abrupt decrease in thickness, and a reduction in reflectance is observed [22].

4. Conclusions

ITO films were deposited on a glass substrate with r.f. magnetron sputtering. The refractive indices of the films are found to decrease with the decrease of sputtering power or increase of the oxygen content in the sputtering ambient. The refraction index n at 550 nm ranges from 1.87 for films prepared at 20 W, 8% O_2 to 2.17 for those prepared at 100 W, 0% O_2. A double layer coating was fabricated on a glass substrate with ITO films of different refractive indices. It is found that the reflectance at 550 nm decreases from $\sim 8.78\%$ of the uncoated substrate to $\sim 5.71\%$ of a $\lambda/4 - \lambda/4$ double layer coating with refractive index of inner ITO film equals 1.87 and that of outer ITO film equals 2.17. Besides, the double layer ITO coating $(\lambda/4 - \lambda/4)$ has lower reflectance than the single layer ITO coating (λ/2) does. Hence, it is feasible to fabricate a multilayer antireflective (AR) coating with a single ITO target by controlling the sputtering parameters. Another approach to a single target ITO AR coating is through microstructure engineering of the ITO surface. However, a breakthrough in the etching technique of the ITO film is required before this approach can be realized. A decrease in reflectance is observed at wavelengths between 800 nm and 1500 nm.

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