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Room-temperature deposition of indium tin oxide thin films with plasma ion-assisted evaporation

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Abstract

The electrical and optical properties of indium tin oxide (ITO) thin films deposited by plasma ion-assisted evaporation are reported. With deposition at room temperature using certain ion-source parameters ITO films with an electrical resistivity of 5×10^{-6} Ω m and an absorptance at 550 nm of less than 5% for 300 nm film thickness were obtained. Variation of oxygen pressure during deposition results in different band gap energies and different resistivities. The complex index of refraction was determined using a dispersion model suitable for explaining the particular properties of ITO in the visible and near infrared spectral range. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Indium tin oxide (ITO); Transparent semiconductors; Ion-assisted deposition

1. Introduction

Indium tin oxide (ITO) belongs to the class of transparent conductive materials. On one hand ITO is an electrical conductor and on the other hand it shows a high transmittance in the visible spectral range. Moreover, a high reflectance in the infrared (IR) range is related to the electrical conductivity. This series of promising optical and electrical properties results from the fact that this material is a n-type degenerated semiconductor with a wide band gap ($E_g\approx4$ eV). For IR radiation ITO acts as a metal-like material due to the high density of free electrons in the conduction band. For light with a wavelength shorter than the electron plasma wavelength ITO is transparent until the fundamental absorption starts at wavelengths close to the corresponding band gap energy. Various applications using the properties of ITO thin films have been introduced [1–3], for instance the use in flat panel displays, transparent heat mirrors, IR and radio frequency protective windows and transparent electrodes for solar cells. Many deposition techniques have been successfully applied to fabricate ITO thin films, most of them requiring elevated substrate temperatures or post-deposition annealing [4–7]. Besides chemical vapour deposition, spray pyrolysis and magnetron sputtering, vacuum evaporation with ion-assistance is gaining considerable respect.

In this paper, we present results of ITO fabrication with plasma ion-assisted deposition using Leybold's advanced plasma-source (APS) [8]. This deposition technique is well-established for producing dense and adhesive dielectric films, even at room temperature.

2. Experimental procedure

ITO films were deposited onto BK7 glass substrates by electron beam evaporation in oxygen atmosphere without substrate heating. The deposition material was a mixture of 90 at.% indium oxide (In_2O_3) and 10 at.% tin oxide (SnO_2) by Merck. During the deposition process the substrate holder was rotated and the substrate surfaces were bombarded by argon ions extracted from a plasma generated by the APS. Discharge voltage and discharge current were 65 V and 40 A, respectively. The deposition rate was varied in the 0.10–0.35 nm/s range and the typical film thickness was 300 nm. The electrical and optical properties of ITO films can be changed by varying the deposition parameters such as deposition rate and oxygen partial pressure as well as the ion source parameters such as ion energy and ion flux. O_2 and Ar content were determined by gas flow controllers and total pressure measurements with vacuummeter.

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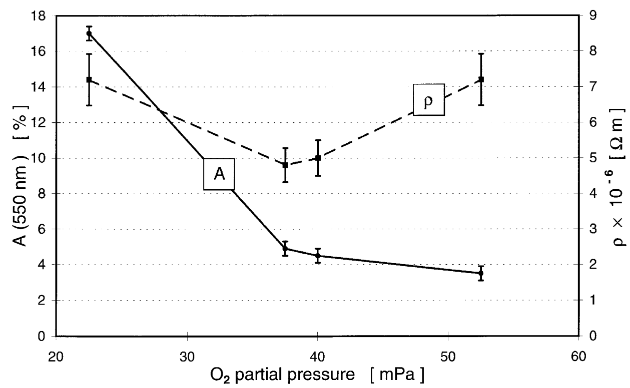


Fig. 1. Optical absorptance A at a wavelength of 550 nm and electrical resistivity ρ vs. oxygen partial pressure during the deposition process.

Four-point probe and Hall effect measurements were used to determine the sheet resistance and the concentration of free charge carriers. Reflectance and transmittance in the 350–2500 nm range were measured with a Perkin–Elmer Lambda 19 spectrometer and reflectance in the 2–20 μm range was measured with a Fourier transform infrared spectrometer FTS 175 by Biorad.

3. Results and discussion

First the variation of electrical resistivity ρ and optical absorptance A in the visible spectral region with oxygen partial pressure was examined. In Fig. 1 ρ and A at a wavelength of 550 nm are plotted versus O_2 partial pressure for a deposition rate 0.10 nm/s. Absorptance was determined from reflectance and transmittance with $A = 1 - R - T$. The electrical resistivity ρ shows a minimum at a certain oxygen partial pressure whereas the absorptance drops monotonously with increasing oxygen content. A significant dependence of resistivity on deposition rate could not be found if oxygen partial pressure was optimized for each deposition rate. Fig. 2 shows ρ vs. deposition rate. The values of ρ vary around 4.4×10^{-6} Ω m for all deposition rates. TEM investigations of ITO film cross sections do not give evidence about distinct differences in grain size, see TEM images in Fig. 3. For deposition rates of 0.17 and 0.35 nm/s quite similar averaged grain sizes of ≈15 nm can be found. For such grain sizes the grain boundary scattering of charge carriers plays an important role in limitation of carrier mobility and thus in limitation of electrical resistivity [9].

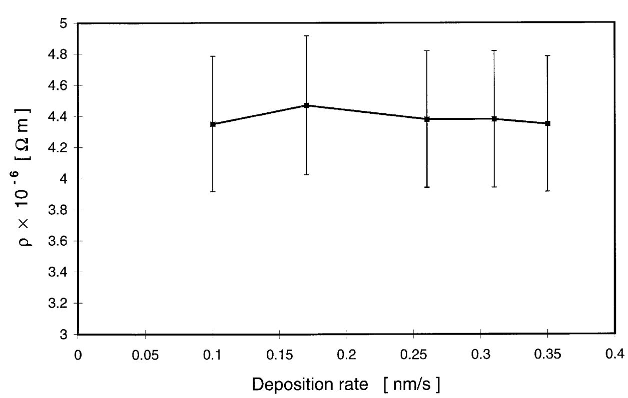


Fig. 2. Electrical resistivity vs. deposition rate.

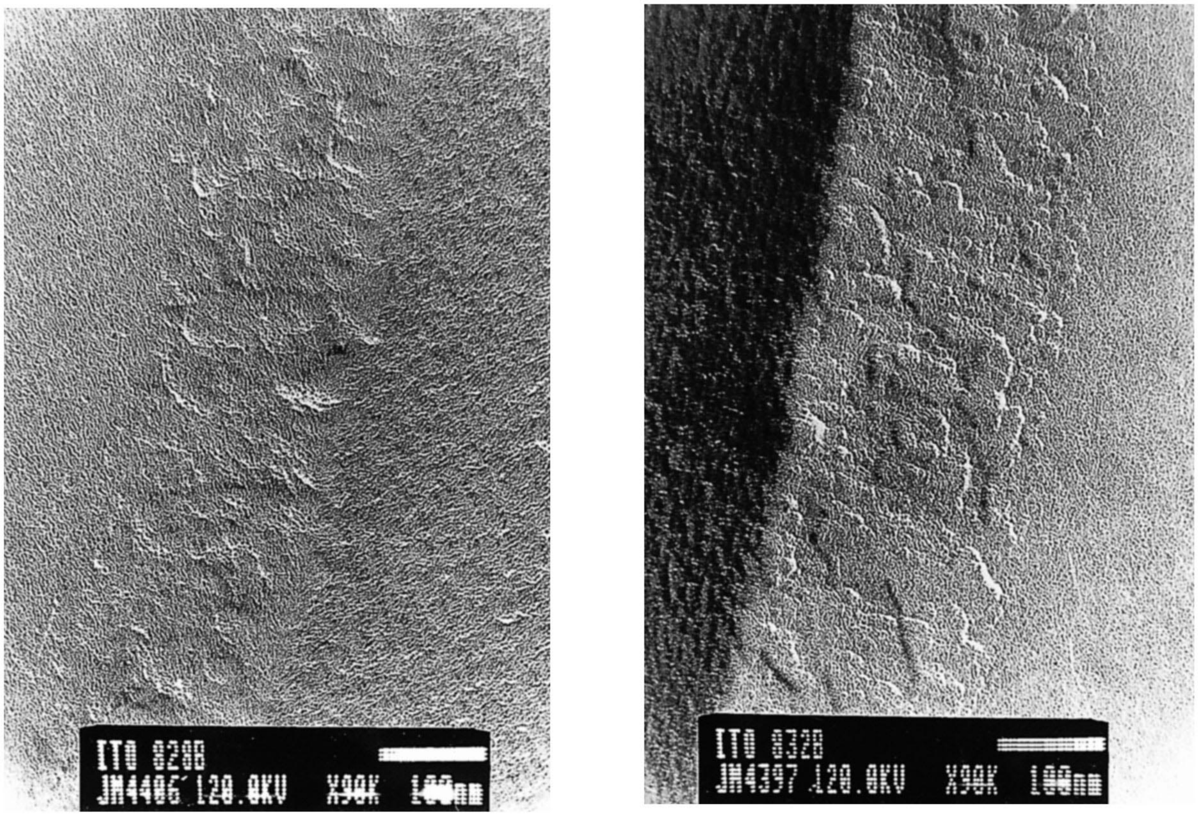
For band gap studies the dispersion of optical absorption coefficient α near band gap energy was evaluated. The plot of $\alpha^{1/2}$ or α^2 versus photon energy gives information about the energy of the indirect or direct band gap of the material, respectively [10]. Fig. 4 shows a plot of $\alpha^{1/2}$ and α^2 versus photon energy. The linear extrapolation of these curves towards the intersection with the x-axis results in an indirect band gap of $E_{\mathrm{indir}} \approx 2.85 \pm 0.12$ eV and a direct band gap of $E_{\mathrm{dir}} \approx 3.75 \pm 0.26$ eV for the ITO film with the resistivity of 4.4×10^{-6} Ω m. The value for direct band energy is quite similar to that referred to by Chopra et. al. [3] or that found by Coutal et. al. for excimer laser evaporated ITO films at elevated temperatures [7]. The influence of oxygen pressure on band gap is shown in Fig. 5. An O_2 partial pressure of 22 mPa results in a widening of the indirect band gap due to Burstein–Moss effect [11,12] by ≈0.25 eV compared with the value obtained at 52 mPa, indicating an increase of carrier concentration by around 2×10^{26} m^{-3} obvious due to more oxygen vacancies in the lower-pressure case. This charge carrier concentration can roughly be estimated from the band gap shift ΔE^{BM}

due to Burstein–Moss effect by using equation:

$$\Delta E^{\mathrm{BM}} = \frac{\hbar^2}{2m_{\mathrm{VC}}*}(3\pi^2 N)^{2/3} \tag{1}$$

with reduced effective mass $m_{VC}* = 0.55m_e$ (m_e mass of the electron), a value typical for ITO [13]. Hall effect measurements showed a carrier concentration of N ≈ 10^{27} m^{-3} for all samples. Thus the carrier mobility is in the $10–20 \times 10^{-4}$ m^2/Vs range. Table 1 shows the indirect band gap energies for ITO films grown with a deposition rate of 0.10 nm/s and different oxygen partial pressures.

The index of refraction and extinction were calculated from reflectance and transmittance measurements by fitting a dispersion model for the complex dielectric function $\varepsilon(\omega)$. The reflectance of ITO films is often described using Drude's model for free charge carriers [14] resulting in useful values of refractive index n. But this model is only a first approximation and fails for calculating the transmittance in the visible range where the light frequency is higher than the plasma frequency of the ITO material. The values of extinction index k for visible wavelengths cannot be used in such cases. To overcome these problems it is necessary to modify Drude's model by adding an additional term, which takes the dielectric behaviour of ITO into consideration. A simple approach to a reasonable solution is an oscillator model often used in the basic theory of solid state physics [15]. So following Hamberg and Granqvist [16] our model



(a) (b)

Fig. 3. TEM images of ITO film cross sections, (a) deposition rate 0.35 nm/s, (b) deposition rate 0.17 nm/s.

of dispersion of complex dielectric function $\varepsilon(\omega)$ is:

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = (n + ik)^2$$

$$= \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \frac{s_o}{\omega_o^2 - \omega^2 - i\gamma\omega} \quad (2)$$

with dielectric constant at high frequencies $\varepsilon\infty$, plasma resonance frequency ω_p, relaxation time τ, oscillator strength s_o, oscillator resonance frequency ω_o and oscillator damping constant γ. Fig. 6 shows the measured reflectance and transmittance curves as well as the curves fitted using Eq. (2). The average deviation of the calculated curves is 1.9% if both reflectance and transmittance are fitted together with the same weight. Fitting each quantity separately in limited spectral regions results in average deviations less than 0.5%. The model parameters for the best fit of both reflectance and transmittance together are summarized in

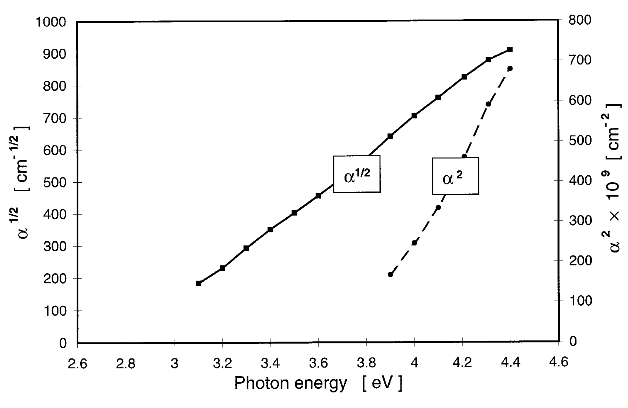


Fig. 4. Optical absorption coefficient $\alpha^{1/2}$ and α^2 versus photon energy for determination of band gap energy.

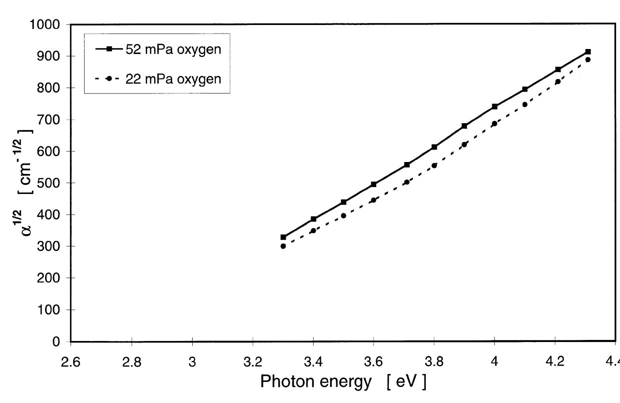


Fig. 5. $\alpha^{1/2}$ versus photon energy, influence of oxygen partial pressure.

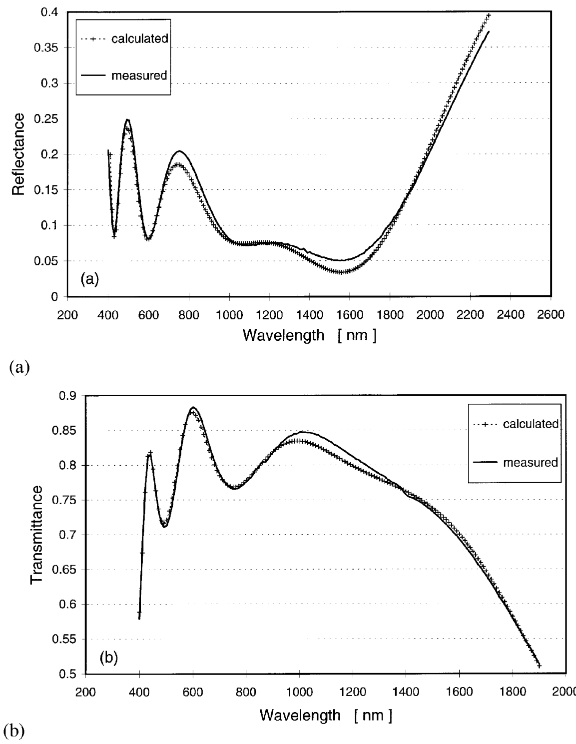


Fig. 6. (a) Reflectance and (b) transmittance of a 300-nm thick ITO film deposited with APS on BK7 glass, measured and calculated by using Eq. (2).

Table 2. The dispersion curves of index of refraction and extinction coefficient resulting from these dispersion parameters are shown in Fig. 7.

4. Conclusion

It was shown that ion-assisted deposition of ITO using APS provides transparent conductive films of low electrical resistivity and high optical transmittance. These excellent properties, comparable with ITO films deposited with conventional evaporation or sputtering at elevated substrate temperatures and post-annealing, can be obtained even if the films are grown at room temperature without any post-deposition treatment. This advantage makes our deposition technique useful too for production of low-resistance ITO films also on organic substrates.

The electrical resistivity of the ITO films strongly depends on the oxygen pressure during deposition. It shows a minimum at certain ratios of oxygen partial pressure to deposition rate, whereas the absorptance in the visible range drops monotonously with increasing oxygen pressure. A minimal resistivity of $\rho = 4.4 \times 10^{-6}$ Ω m and an absorptance of $\leq$5% at a wavelength of 550 nm could be obtained. The influence of oxygen content on band gap energy was investigated and showed a band gap widening by about 0.1 eV due to slight O_2 deficiency.

The index of refraction and extinction were determined in the entire visible and the NIR range using a dispersion model that combines metal like behaviour following Drude's model with dielectric behaviour described with an oscillator. This model fits well the measured reflectance and transmittance data in the spectral range of interest.

Table 1
Indirect band gap energies of ITO films deposited with a deposition rate of 0.10 nm/s

Oxygen pressure (mPa)	Indirect band gap energy (eV)
22	2.97±0.11
37	2.85±0.12
52	2.73±0.07

Table 2
Characteristic parameters of a combination of Drude's model with oscillator for dispersion of complex dielectric function, for explanation see text

$\varepsilon\infty$	ω_p (rad/s)	τ (s/rad)	s_o	ω_o (rad/s)	γ (rad/s)
3.57	1.89×10^{15}	6.34×10^{-15}	0.49	5.61×10^{15}	9.72×10^{13}

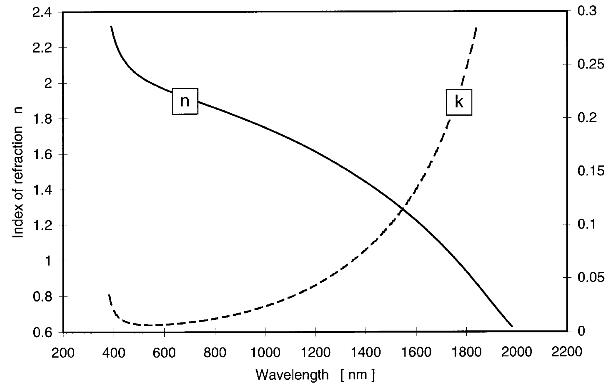


Fig. 7. Index of refraction n and extinction coefficient k of ITO deposited with APS, deposition rate 0.10 nm/s, oxygen pressure 37 mPa.

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