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Effects of air annealing on the optical, electrical, and structural properties of indium-tin oxide thin films

C. Trejo-Cruz [a], A. Mendoza-Galván [a,*], A.M. López-Beltrán [a,b], M. Gracia-Jiménez [c]

[a] Cinvestav-Querétaro, Libramiento Norponiente 2000, Fracc. Real de Juriquilla, 76230 Querétaro, Mexico
[b] Facultad de Ciencias Químico-Biológicas, Universidad Autónoma de Sinaloa, Ciudad Universitaria, 80010 Culiacán, Mexico
[c] Instituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Mexico

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ABSTRACT

The effects of air annealing on the optical, electrical, and structural properties of indium-tin oxide thin films were investigated using spectroscopic ellipsometry in the UV–visible range, reflectance–transmittance spectra at normal incidence in the infrared range, electrical resistivity measurements, and X-ray diffraction. It was found that annealing at 300 °C produces an overall shift to lower photon energies of the optical constant spectra, which is related to the increase in electrical resistivity. The electrical measurements performed in the 25–300 K range show a metallic behavior with large residual resistivity, quantity that increases with annealing temperature and is closely related with the change in the relative intensity of the main diffraction peaks. Also it is shown that under certain conditions of film deposition onto indium-tin oxide, some of its properties can change in a similar way as in air-annealing processing.

1. Introduction

Currently, indium-tin oxide (ITO) thin films are used in several applications like flat panel displays, solar cells, electrochromic and energy-efficient windows, among others. However, there are still some aspects on its electronic and optical properties that from both, fundamental and technological, points of view are not well understood and more knowledge should be gained [1–4]. Although the optical properties of ITO films have been reported using spectroscopic ellipsometry [5–8] or reflectance and transmittance spectra [9–11], these studies have been limited either to a certain spectral range or do not include effects of thermal annealing. In those works, several dispersion relations Lorentz and Drude based, together with multilayer models and effective medium expressions of different complexity have been used to represent the optical response of ITO films [5–9]. Also, infrared reflectance has been used to study the relationship between carrier concentration, plasma frequency and sheet resistance of polycrystalline and nanoparticle ITO films [9,11]. Other more recent works have reported the effects of annealing on the ITO electrical and optical properties, but these studies were devoted to improve the properties in either vacuum or a N_2 atmosphere [12–14].

In the case of electrical properties, there is a lack of available temperature-dependent resistivity measurements for ITO films, which undoubtedly are valuable because information on the conduction mechanism can be extracted [2,9]. Since temperature is a source for ITO degradation and consequently device failure [3], the effect of annealing on the temperature-dependent electrical properties is of great interest. Furthermore, as applications of ITO films include the deposition of coatings with specific properties (spectral selectivity, transparency, etc.), it is of importance to evaluate the effect of annealing on the ITO optical properties in a wide spectral region. In this work, the optical constants of ITO films are reported in a wide spectral range together with resistivity measurements at low temperatures. In this way, the effect of air annealing on film properties ranging from ultraviolet wavelengths to dc is studied in a unified scheme and extended to include changes in the structural properties. Also, it is shown that similar effects to air annealing on the ITO properties can be unintentionally produced when techniques like sputtering are used to deposit films onto ITO. This should be considered for a precise device characterization.

2. Experimental details

ITO films with a sheet resistance of 10 Ω □ deposited on Corning 1737 aluminosilicate glass slides, as specified by the supplier (Delta Technologies, Ltd.), were annealed in air at temperatures in the range of 100–500 °C for 1 h. The glass substrate was characterized etching the ITO film by using an aqueous solution of HCl and HNO_3 for 40 min. After this, the glass slide was immersed in an aqueous solution of Na_2CO_3, cleaned in deionized water with ultrasound stirring and finally dried with nitrogen gas.

The optical properties were investigated using variable angle spectroscopic ellipsometry (SE) measurements in the spectral range of 1.5–5.0 eV and reflectance–transmittance spectra in the infrared range. SE measurements were performed at incidence angles of 60, 65,

* Corresponding author. Tel.: +52 442 211 99 22; fax: +52 442 211 9939.
E-mail address: amendoza@qro.cinvestav.mx (A. Mendoza-Galván).

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and 70°, with a phase modulated ellipsometer (Jobin Yvon Uvisel DH10). For these SE measurements, the back side of the glass substrate was roughened to avoid back reflection, which introduces spurious non-polarized light in the probe beam.

SE measures the change in the polarization state of a light beam when it is reflected from a sample. Such change is determined by the complex reflectance ratio between the Fresnel coefficients for polarization parallel (r_p) and perpendicular (r_s) to the incident plane, and is expressed in a parametric form by the ellipsometric angles Ψ and Δ through the relation [15],

$$\tan \Psi e^{i\Delta} = \frac{r_p}{r_s}. \quad (1)$$

Thus, theoretical ellipsometric spectra can be calculated from the construction of an optical model for the coefficients r_p and r_s, which are compared to experimental data by a regression fitting procedure. This allows to determinate thicknesses and optical constants of various films in multilayered samples.

Infrared measurements were performed with a Bruker Optics Equinox 55 system. For reflectance spectra at near normal incidence, the specular accessory was used with an optical quality gold sample as reference. Transmittance spectra at normal incidence were available only in the near infrared range due to absorption of glass substrate at longer wavelengths. Also, reflectance and transmittance spectra at normal incidence were acquired in the UV–visible spectral range of 240–840 nm with a thin film metrology system (Scientific Computing International, Inc.). The electrical resistivity was measured from room temperature down to 25 K by the van der Pauw method in a cryogenic system attaching copper wire electrodes to the ITO films with silver paste. Atomic force microscopy was used to evaluate the surface roughness in a scan area of 5 μm × 5 μm using a Veeco Dimension 3100 Nanoscope IV in the contact mode with a silicon nitride tip (Veeco NanoProbe™ Model DNP-S10). X-ray diffraction data were acquired with a Rigaku/Dmax-2100 system provided with a thin film accessory at an angle of incidence of 1.5° from sample surface using copper radiation (0.154 nm).

3. Results and discussion

3.1. Optical properties

Fig. 1 shows the experimental and best fit ellipsometric spectra for two films: one not annealed and other annealed at 300 °C. Spectra are for the incident angle of 65°, continuous lines correspond to experimental spectra and discontinuous lines to the best fit. The latter were obtained using an air–rough layer–ITO film–glass substrate system. For that, the ITO optical constants were modeled using a generalized Lorentz oscillator expression considering the parameters of two oscillators [16]. The optical constants of glass were obtained from SE measurements carried out on a bare substrate. For the roughness layer the Bruggeman's effective medium expression with a 50%–50% mixture of voids and ITO was considered as is usual for modeling SE data [15]. The measured data at the three angles of incidence were simultaneously fitted, obtaining a film thickness of 130 nm and a rough layer 3 nm thick for the not-annealed film. The latter value is in good agreement with the rms roughness of 2.7 nm obtained from atomic force microscopy. The resulting optical constants for ITO will be discussed below.

As is known, for a transparent or weakly absorbent film (which is expected for ITO films in the visible range) interference cause maxima and minima in Ψ spectra at wavelengths where the phase factor β is a multiple integer of π [15],

$$\beta = 4\pi \left(\frac{d}{\lambda}\right) \sqrt{N_f^2 - n_a^2 \sin^2 \phi}, \quad (2)$$

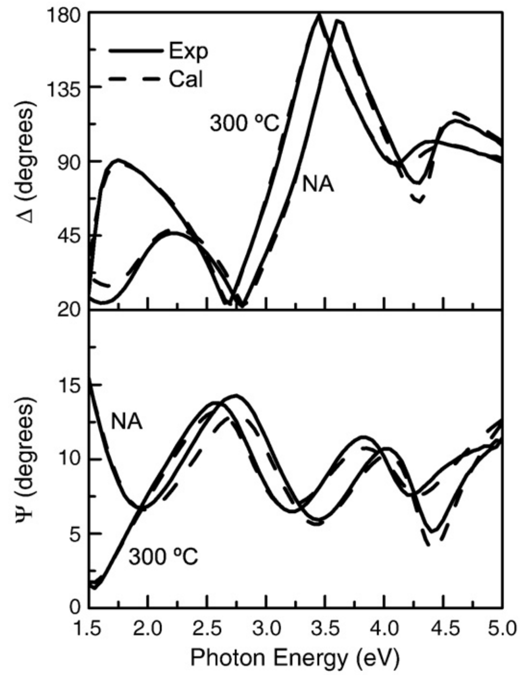

Fig. 1. Experimental and best fit ellipsometric spectra of not-annealed (NA) and annealed at 300 °C ITO films.

where d and N_f ($=n+ik$) are the ITO thickness and complex refractive index, respectively, $n_a=1$ the refractive index of air, ϕ is the angle of incidence, and λ the wavelength of incident light. It should be noticed in Fig. 1 that the main effect of annealing on SE data is the shift to lower photon energies in the spectral position of the maxima and minima in Ψ as well as the shift of the abrupt change in Δ spectra at about 2.7 and 3.5 eV. According to Eq. (2), such shift would imply an increase in either film thickness or refractive index. Because the former case is unlikely, the shift in spectra after annealing is due to the change in the complex refractive index of the ITO film. In fact, the fitting procedure reported nearly the same value of film thickness for both, not-annealed and annealed samples. However, the roughness layer thickness increased from 3 nm to 5.6 and 8.7 nm after annealing at 300 and 500 °C, respectively. Such increase in the surface roughness is related to the increase in grain size with annealing temperature as determined from X-ray data. That is, values of 24, 28, and 32 nm of the grain size were obtained for not annealed, annealed at 300 and 500 °C, respectively. In Fig. 1 it is noteworthy that all the features in experimental spectra are well reproduced by the fitted data, which supports the reliability of the resulting optical constants.

The UV–visible–IR transmittance (T) and reflectance (R) experimental spectra for several samples are shown in Fig. 2. For clarity purposes, the spectra are shown only for wavelengths shorter than 8 μm and the change in scale at 0.85 μm should be noticed. In Fig. 2 the steep decrease in T at about 0.3 μm is largely influenced by absorption of the glass substrate. Because the band gap of ITO is located around this range, its precise determination would be difficult from T spectra alone. That was one reason why we used SE to obtain ITO optical constants in the UV–visible range because as a reflection probe, light traveling through the substrate does not influence the measurement. In this range, both T and R spectra clearly show interference oscillations, which shift to longer wavelengths with annealing, in agreement with the shift already discussed for SE spectra of Fig. 1. In fact, the dotted R and T spectra of Fig. 2 in the range of 240–840 nm were calculated with the model and parameters obtained in the analysis of SE data. It should be noticed that the annealing shifts the transparency window (between 0.4 and 1 μm) to longer wavelengths. Regarding the infrared range in Fig. 2, the R spectra show the