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Spectroelectrochemical properties of ultra-thin indium tin oxide films under electric potential modulation

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ABSTRACT

In this work, the spectroscopic properties of ultra-thin ITO films are characterized under an applied electric potential modulation. To detect minute spectroscopic features, the ultra-thin ITO film was coated over an extremely sensitive single-mode integrated optical waveguide, which provided a long pathlength with more than adequate sensitivity for optical interrogation of the ultra-thin film. Experimental configurations with broadband light and several laser lines at different modulation schemes of an applied electric potential were utilized to elucidate the nature of intrinsic changes. The imaginary component of the refractive index (absorption coefficient) of the ultra-thin ITO film is unequivocally shown to have a dependence on the applied potential and the profile of this dependence changes substantially even for wavelengths inside a small spectral window (500–600 nm). The characterization technique and the data reported here can be crucial to several applications of the ITO material as a transparent conductive electrode, as for example in spectroelectrochemical investigations of surface-confined redox species.

1. Introduction

Because of its good optical transparency and electrical conductivity, films of indium tin oxide (ITO) have been widely used in solar cells [1–3], displays [4,5], electrochromic devices [6,7], LEDs [8–10], and spectroelectrochemical applications [11,12]. ITO films in the thickness range of about 100 nm to 1 μm that had been grown by different deposition techniques and treated under diverse annealing conditions have been extensively investigated [13–16]. The conductivity and transparency of these films, and their relationship to the film crystalline structure have been widely studied [13]. However, those studies have been implemented for relatively thick ITO films (above 100 nm) because it becomes particularly challenging to characterize the spectroscopic features of thinner (e.g., below 30 nm) ITO films. The optical transparency and spectroscopic features of very thin ITO films cannot be precisely addressed by conventional transmission measurements and advanced characterization techniques are required in these cases. Another important limitation has been the lack of information on how the spectroscopic properties of the ITO film behave under potential modulations, which is crucial to understand the performance of those films at working conditions in a variety of applications. Only a few studies have been reported on the electrical properties of ITO films under potential modulations in different solution and electrolyte conditions [17–20], and on the refractive index of ITO films under potential modulation [21,22], however those studies were limited to relatively thick ITO films.

In this present work, we apply an integrated optical waveguide technique to study the spectroscopic optical characteristics of ultra-thin ITO films. A planar, single-mode, integrated optical waveguide (IOW) creates a highly sensitive platform to investigate the spectroscopic properties of an overcoated ultra-thin ITO film. We report here investigations on the spectroscopic properties of ultra-thin ITO films performed under aqueous environment and different electric potential modulation approaches, which represent the working conditions present in many of the applications of ITO films. It is expected that the electrical modulation and environmental conditions will have a stronger impact in the properties of thinner films, as opposed to the thicker ones, and we aimed to address those effects in this work. Understanding the spectroscopic features of ultra-thin ITO films under those conditions is particularly critical for spectroelectrochemical and electro-optical applications that utilize an ITO film as a transparent working electrode [23].

2. Thick ITO films

2.1. Sample preparation

The ITO fabrication process was first optimized to create films with extremely low optical attenuation and good electrical conductivity. For this purpose, relatively thicker ITO films (ca. 400 nm) were deposited on plain glass slides to identify the best fabrication conditions. Once those conditions were established, such protocol was then applied to

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deposit ultra-thin ITO films (ca. 13 nm) over single-mode IOW devices described in Section 3.

A pulsed-DC sputtering technique was used to deposit ITO films from a 3-inch target of $(In_2O_3)90{:}(SnO)10$ wt.% and 99.99% purity. The power of the pulsed-DC sputtering was set at 200 W with a frequency of 20 kHz and a pulse duration of 1 μs. The substrates were kept at room temperature during deposition and the rotation speed of the substrate table was set at 20 rpm to achieve uniform films. The flow rate of Ar was fixed at 12 sccm and different flow rates of O_2 were explored (0.4 sccm to 0.8 sccm) to optimize the electrical and optical properties of the ITO film. For each O_2 flow rate, a 30-min deposition process was used to grow a film with a thickness of approximately 400 nm. After the deposition process, an inert annealing treatment in N_2 atmosphere at 250 °C for 10 min was used to activate Sn element, create additional oxygen vacancies, and minimize grain boundary effects to obtain lower resistivity and better transparency in the visible range [24].

2.2. Optical and electrical properties

Transmittance spectra of the thicker ITO samples were measured by a conventional spectrophotometer (Cary 300, Varian). An envelope technique [25] based on the transmittance spectra was employed to determine the thickness and refractive index (both real and imaginary parts) of the ITO films. The sheet resistance and thickness of the film were then used to calculate the film resistivity. In Fig. 1(a) and (b), the extinction coefficient (imaginary part of the refractive index) at the 550 nm wavelength and the resistivity are shown against the O_2 flow rate during the sputtering deposition process. And those properties are compared for samples as sputtered and after the inert annealing treatment.

For the optical performance of samples before the inert annealing process, we observe in Fig. 1 (a) that the extinction coefficient decreases as the O_2 flow rate increases from 0.40 to 0.65 sccm, and remains approximately constant above 0.65 sccm. The inert annealing process substantially reduces the extinction coefficient for samples deposited under low O_2 flow rate (i.e. high values of the extinction coefficients), while the minimum extinction coefficient was found with an O_2 flow rate of about 0.6 sccm. For the electrical resistivity (see Fig. 1b), we notice that regardless of the O_2 flow rate during deposition the inert annealing process consistently improves the electrical conductivity of the film probably by minimizing grain boundary defects in the films [26]. However, when the O_2 flow rate increases, the electrical performance of annealed samples shows a monotonic increase in their resistivity. A flow rate of 0.6 sccm for the O_2 gas during the sputtering process to deposit ultra-thin ITO films was established based on these measurements.

3. Ultra-thin ITO films

3.1. Sample preparation

Planar, single-mode, integrated optical waveguide platforms have been used in challenging studies of adsorbed molecular thin films [27–30] due to their long effective pathlength. The strong optical interaction of a guided mode with a surface-adsorbed molecular assembly has enabled highly sensitive studies of weakly absorbing structures. Fig. 2 schematically shows the IOW structure employed in this work to investigate the spectroscopic properties of ultra-thin films of the ITO material. Two surface-relief gratings (25.4 mm apart from each other) with a pitch size of 323 nm were initially fabricated on glass substrates (75 × 25 mm) to work as integrated waveguide couplers. A highly transparent, single-mode, planar IOW device was created on those glass slides by depositing a 400-nm layer of Al_2O_3 and a 16-nm layer of SiO_2 using an atomic layer deposition (ALD) process. Details of this fabrication process have been reported by us in the literature [30].

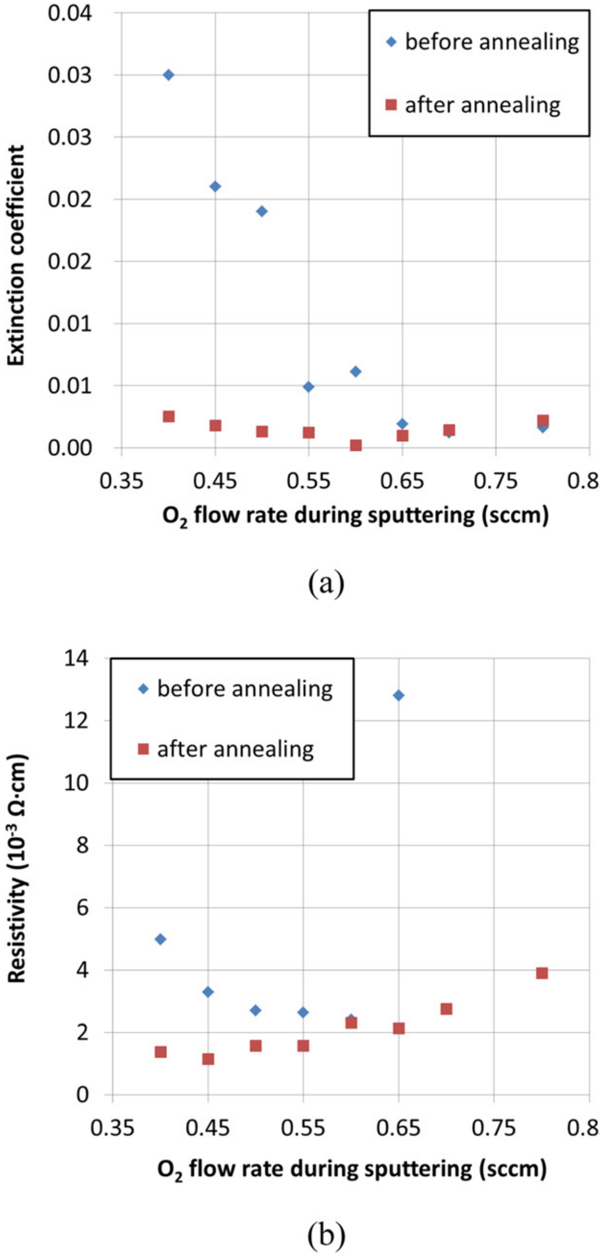

Fig. 1. Effects of O_2 flow rate during the sputtering deposition process on the optical and electrical properties of the ITO film with data provided for measurements before and after an inert annealing treatment. Experimental data of (a) the extinction coefficient (imaginary part of the refractive index) at 550 nm, and (b) the electrical resistivity. As the resistivity before the annealing process is very high at increased levels of O_2 flow rate, the measured resistivity data at 0.70 sccm (2.7 Ω cm) and 0.80 sccm (not conductive) are not displayed in Fig. 1b.

Based on the experimental results described in Section 2 for the (relatively) thicker ITO films, a flow rate of 0.6 sccm for the O_2 gas was selected to deposit a 13-nm ITO film over single-mode IOW devices. After deposition, the same inert annealing process (previously described) was carried out for the ultra-thin ITO films, which provided films with consistently low resistivity values ($\rho = 2.3 \times 10^{-3}\ \Omega\ \text{cm}$). However, the extinction coefficient did not decline to the expected value ($k = 1.7 \times 10^{-4}$) and an annealing process in the presence of O_2 (called reactive annealing) was added to increase the optical transparency of the ultra-thin ITO films in the visible region. By annealing the samples in the presence of atmospheric oxygen, it is expected that oxygen vacancies in the film to decrease leading to a more complete stoichiometry in the ITO film. The fewer defects in the film should translate