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Investigations of electrical and optical properties of functional TCO thin films*

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Transparent conducting oxide (TCO) films of indium-tin-oxide were evaporated on the surface of silicon wafers after phosphorous diffusion and on the reference glass substrates. The influence of deposition process parameters (electron beam current, oxygen flow and the substrate temperature) on optical and electrical properties of evaporated thin films were investigated by means of resistivity measurements and optical spectrophotometry. The performance of prepared thin films was judged by calculated figure of merit and the best result was obtained for the sample deposited on the substrate heated to the 100 °C and then removed from the deposition chamber and annealed in an air for 5 minutes at 400 °C. Refractive index and extinction coefficient were evaluated based on measured transmission spectra and used for designing of antireflection coating for solar cell. The obtained results showed that prepared TCO thin films are promising as a part of counter electrode in crystalline silicon solar cell construction.

Keywords: *transparent conducting oxide; crystalline silicon solar cell; transparent counter electrode.*

1. Introduction

The group of Transparent Conducting Oxides (TCOs) constitutes an unusual class of materials that combine sufficiently large energy band gap (i.e. >3.1 eV), with sufficiently high concentration of electrical carriers (usually in the range of 10^{15} to 10^{20} cm^{-3}), and a sufficiently large mobility (usually several tens of $cm^2 \cdot V^{-1} \cdot s^{-1}$). As a result, a relatively high optical transmittance (usually over 80 %) and low (below 10^{-3} $\Omega \cdot cm$) resistivity can be obtained. Development in this field brought a lot of successful applications of TCOs, mainly as transparent electrodes in, e.g., flat panel displays, touch panels, transparent heaters and solar cells [1, 2]. Moreover, these films can be used equally well in transparent transistors, UV-Vis light emitting diodes and solar cells consisting of a transparent counter electrodes. Besides high transmittance over visible range and high electrical conduction, the TCO thin films often should fulfill other functions. For example, if applied as a part of transparent counter electrode in a silicon solar cell, the TCO thin film should match the requirements for low reflection coefficient (antireflection (AR) coating) and good surface passivation [3]. High electron concentration observed in TCO thin films results in enhanced reflection in near infrared light range. That, in turn, can be a very useful feature for designing of functional coating working as a ”hot” reflector that may protect the cell from its heating when exposed to solar radiation.

One of the most known TCOs is indium-tin oxide compound (ITO), which was developed in the mid-50s last century. In following years many other oxide materials have also been developed, mostly based on indium, tin and zinc oxides. Indium-tin-oxide is the solid state solution of In_2O_3 and SnO_2 in the 90/10 wt.% proportion. However, transparency and electrical performance of

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this compound in the form of thin films are strongly dependent on deposition process parameters, connected with a particular applied technology and with the post deposition treatment. The ITO thin films can be manufactured using different deposition techniques, from which the most common are the magnetron sputtering [4], thermal evaporation [5] and pulsed laser deposition [6].

For the purpose of the present work, the TCO thin films of ITO were deposited using electron beam evaporation (EBE) on the surface of silicon wafers and on the reference glass substrates. Using this technique, the ITO thin films can be obtained by evaporation of In–Sn alloy in the form of small (few millimeters) granules placed in a crucible under a pressure of typically 0.1 Pa, while the vacuum chamber is supplied with oxygen. The oxygen flow and the deposition rate (that is mainly affected by the electron beam current) are the most important factors that determine the transparency and the electrical performance of deposited ITO thin films. If the deposition rate is too high (EB current too high) and the oxygen flow is too low, the resulted thin film will be well conductive, however, it will be opaque to the visible light. On the other hand, if the oxygen flow is too high, the resulted thin films can be well transparent, however, non-conductive. Therefore, the process parameters should be selected individually for almost every type of deposition case.

Another factors that strongly influence the above mentioned thin films parameters are the deposition temperature and application of post-deposition annealing. It is commonly known in coating technology that an increased substrate temperature strongly influences the microstructure of deposited thin films, therefore, also influences many other, e.g., optical, electrical or mechanical properties of the deposited thin films [7].

In this paper, some exemplary results of electrical and optical investigations performed on ITO thin films, deposited and then treated in different conditions, are described. Optical investigations, besides the measurements of the transmittance of the deposited thin films, included reflectance measurements of the thin films deposited on standard crystalline silicon substrates used in solar cells production. The obtained results are promising for application of the developed deposition parameters for ITO thin films for the fabrication of counter electrodes in new design of crystalline silicon solar cells construction.

2. Experimental

The ITO thin films were deposited using electron beam evaporation (EBE) process on the surface of crystalline silicon wafers and on the reference glass substrates. The silicon substrates were much the same as that used for solar cells production, i.e. p-type silicon wafers were already after phosphorous (n-type) diffusion, ready for deposition of passivation layer and electrical contact metallization. Before deposition of ITO thin films, the wafers were etched in a standard HF solution in order to remove the native SiO_2 layer. The 90/10 ITO, 99.99 % grade, high density black granules were evaporated from a tungsten boat under the electron beam acceleration voltage of 7 kV in 400 L vacuum chamber evacuated first to the base pressure of 0.5 Pa and then filled with the oxygen (99.999 % purity) to the working pressure of 0.1 Pa.

Optical properties were verified by transmission and reflection measurements using the setup built from QE65000 optical fiber spectrophotometer, the coupled deuterium-halogen lamp and integration sphere. Electrical properties were investigated using a standard co-linear Jandel four point probe supplied by Keithley 2601 Source Metter.

At first, preliminary deposition tests were performed in order to determine the required oxygen flow and the electron beam current. The set of three thin films were deposited for 3 minutes: P1 (25 mA and 10 sccm O_2), P2 (20 mA and 50 sccm O_2), P3 (15 mA and 30 sccm O_2). Fig. 1 presents transmittance characteristics and the results of electrical measurements of ITO thin films deposited on cold (not heated) substrates under different oxygen flow and with different value of electron beam (EB) current. The transmittance (T_{550}) was determined for 550 nm wavelength.

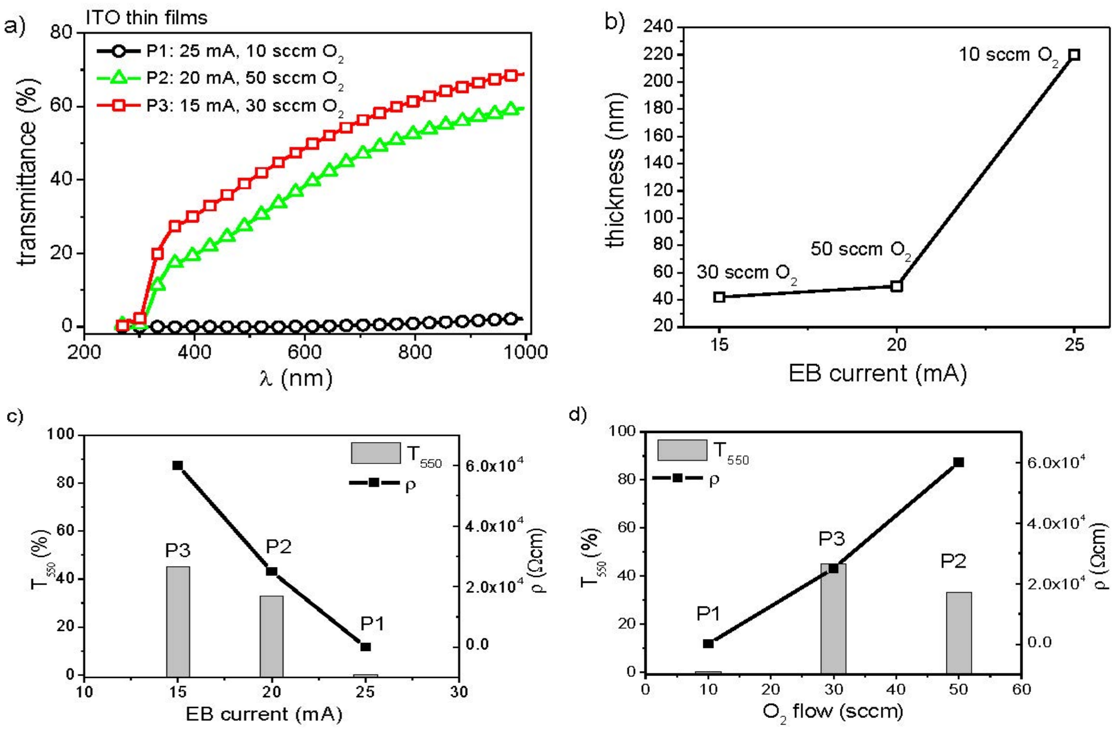

Fig. 1. Transmittance characteristics (a), thickness vs. electron beam current (b) transmittance at the 500 nm wavelength and resistivity of ITO thin films deposited on glass substrates at different electron beam currents (c) and under different oxygen flows (d).

Analysis of obtained preliminary results (Fig. 1) indicates that a compromise must be reached between the oxygen flow and electron beam current. The best compromise was achieved for 30 sccm oxygen flow and the current equal to 20 mA. For these selected process parameters, four sets of samples were prepared under different technological conditions and their preparation details are listed in Table 1. The substrates were heated during deposition using radiation heaters. The thickness of the films was controlled in-situ using a FTC-2800 quartz thickness controller. After the deposition, samples were additionally heated in two ways: selected samples (S1, S2) were first annealed in the deposition chamber filled with O_2 to the pressure of 2 Pa (Table 1) and left there for several minutes, while samples S3 and S4 were immediately removed from the chamber after the deposition. Then all samples were heated for 5 minutes on the hot plate at 400 °C in ambient air.

3. Results

Prepared thin films, directly after deposition, were semitransparent and additional heating in air ambient was required to increase their transparency. Fig. 2 and Fig.3 present results of optical investigations of all thin films deposited on glass (Fig. 2) and silicon (Fig. 3) substrates before and after additional post deposition annealing in air. For convenience, the annealed samples are denoted with ”A”.

Directly after deposition, the samples were semitransparent and the shape of all measured curves was quite similar. After additional annealing in air, with exception of the S4 sample, transmission coefficient increased over the whole investigated visible spectrum range and reached ca. 80 % (Fig. 2b). Performed reflection measurements (Fig. 3) testify about good antireflection properties of ITO thin films when deposited on

Table 1. Technological process parameterers of preparation of as-deposited ITO thin films.

Sample	Thickness (nm)	Substrate temperature during deposition (°C)	Time of additional heating in the deposition chamber (min)
S1	120	330	15
S2	30	100	5
S3	50	100	–
S4	65	60	–

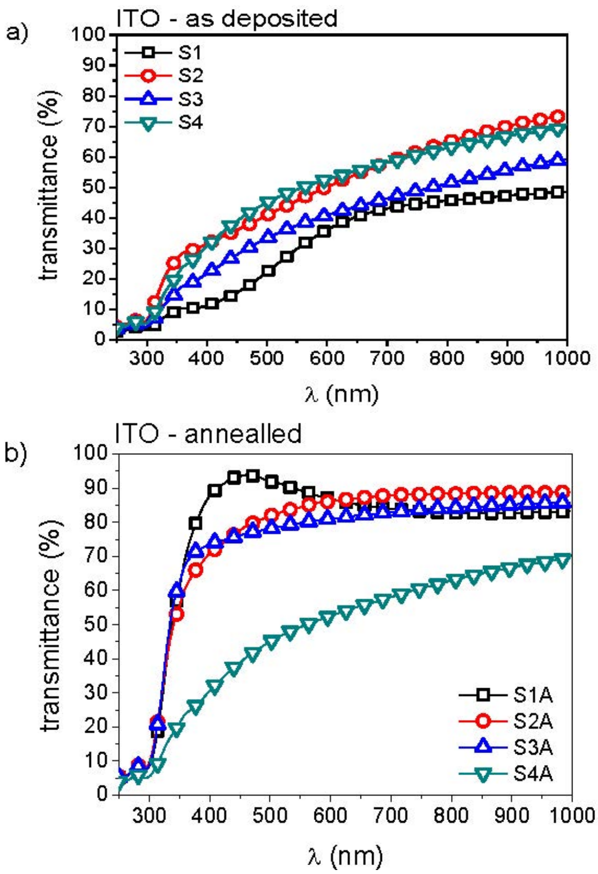

Fig. 2. Optical transmittance characteristics of ITO thin films deposited on glass: (a) before and (b) after additional annealing in air for 5 min at 400 °C.

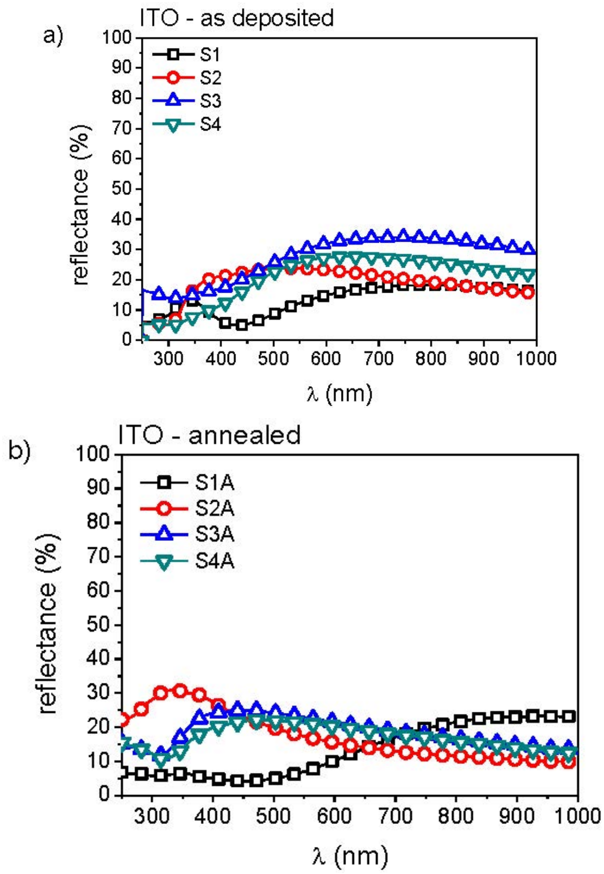

Fig. 3. Optical reflectance characteristics of ITO thin films deposited on the substrate of crystalline silicon wafers: (a) before and (b) after additional annealing in an air for 5 min at 400 °C.

silicon substrate. For a single thin film antireflection coating, the position of a minimum reflectance point is dependent on the thin film thickness and on the refraction index of deposited thin film material. Therefore, in order to select the process parameters for which such structures would have the best performance, refraction index spectra were developed and analyzed for the annealed thin films. Fig. 4a and 4b presents dispersion spectra of refraction (n) and extinction (k) coefficients. The spectra were evaluated using SCOUT software [8].

As it can be concluded from Fig. 4, thin films deposited on the substrates heated to at least 100 °C (S1 – S3) are low absorbing and over ca. 400 nm they are characterized by well defined,

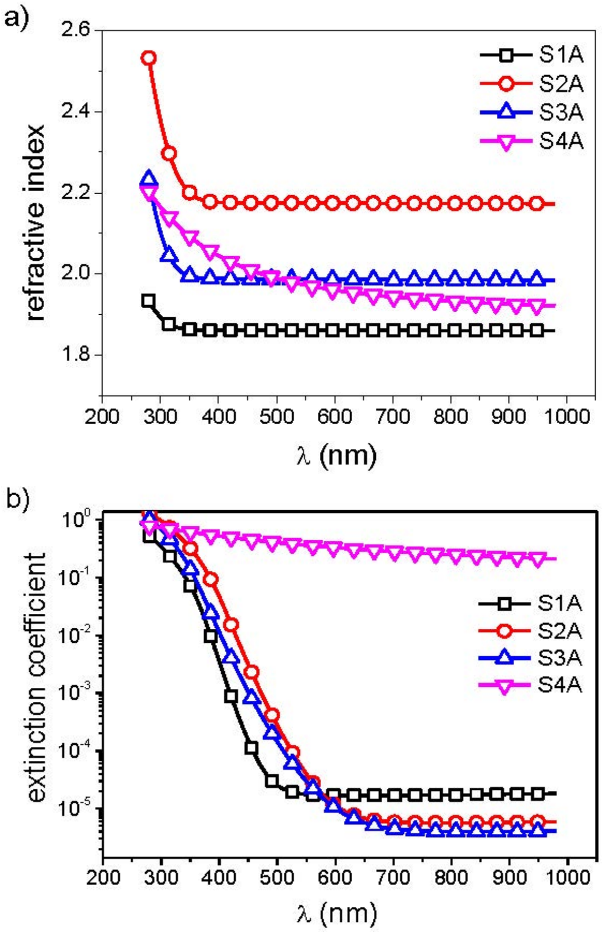

Fig. 4. Dispersion spectra of: (a) refractive and (b) extinction coefficients evaluated for additionally annealed ITO thin films.

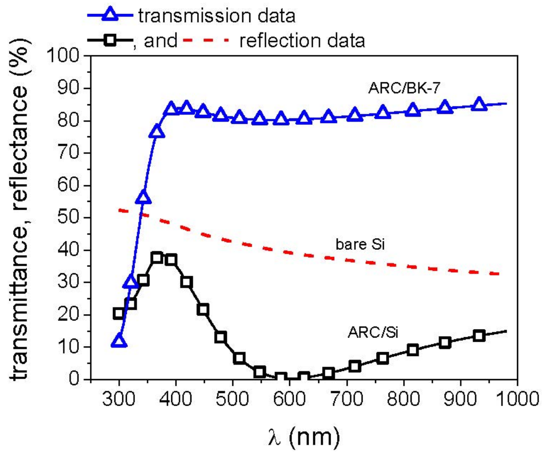

Fig. 5. Transmission (a) and reflection spectra (b) elaborated based on n and k results for S3 sample thin film deposited on standard glass (Schott BK-7) and silicon substrates.

flat-shape refractive index spectral dependence. Higher deposition temperature (340 °C) for sample S1A resulted in its lower refraction index value. An optimal material for a single thin film AR coating should have the refractive index value between surroundings and the substrate [7]. In case of air as surroundings (n = 1) and silicon as a substrate (n = 3.8 at 550 nm), the optimum refractive index value should be n = 1.95. The closest value from elaborated n(λ) spectra (Fig. 4a) can be find for the S3 thin film (n = 1.98), which was deposited at 100 °C, removed from the chamber directly after the deposition and then additionally annealed in air.

The results of electrical measurements performed on prepared samples are summarized in Table 2. The lowest resistivity directly after deposition displayed the S1 thin film, deposited on the substrates heated to 340 °C and additionally annealed in the deposition chamber for 15 min. However, the best conductivity after additional annealing in air was observed for the S3 sample.

Overall performance of different TCO thin films can be verified using the figure of merit similar to that proposed by Haacke [9]:

$$\varphi = \frac{T_{\lambda}^{10}}{\rho}, \tag{1}$$

where: T_{λ}^{10} – optical transmission coefficient at selected wavelength λ (600 nm in this work), ρ – thin film resistivity in Ω·cm.

Values of the *figure of merit* calculated for all prepared samples are collected in Table 2. The best performance was found for the S3 sample which also had the lowest resistivity, transparency of about 81 % at the wavelength of 600 nm and the optimum refractive index for AR coating on silicon substrate. Fig. 5 presents simulated transmission and reflection spectra for a single layer AR coating designed based on the results elaborated for the S3 sample thin film, deposited on a standard glass (Schott BK-7) and silicon wafer substrates, respectively.

Table 2. Electrical properties of ITO thin films prepared under different technological conditions and after additional post-process annealing in an air.

sample \ property	S1	S2	S3	S4	S1A	S2A	S3A	S4A
$\rho(\Omega\cdot cm)$	59.82×10^{-3}	543.6	113.5	13.55	3.24	1.09×10^{-3}	4.53×10^{-4}	0.12×10^{-3}
$\varphi(\Omega^{-1}\cdot cm^{-1})$	6.11×10^{-4}	1.57×10^{-6}	1.30×10^{-6}	$1.29\ 1\times 10^{-4}$	0.08	174	271.71	14.57

Optimum thickness of the ITO thin film should be about 71 nm, which is equal to one quarter wave optical thickness of the given ITO: the S3 thin film at the designed wavelength of 600 nm.

4. Conclusion

The results showed the major influence of an additional substrate heating during and after the deposition process of the ITO thin films on their electrical an optical performance. The best performance was found for the thin film deposited on the substrates heated up to 100 °C and after additional annealing in air at 400 °C for 5 min. The obtained results proved that the prepared ITO thin films can simultaneously be considered as antireflective coatings, which indicates their possible use as a part of functional counter electrodes in silicon solar cells construction.

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