The influence of material parameters on optical and electrical properties of indium-tin oxide (ITO) layer

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Abstract. Indium tin oxide (ITO) layers of various thicknesses were deposited on silicon substrate using magnetron sputtering technique. The use of the layers is dedicated to solar cells produced on the basis of heterostructures at low range of temperatures up to 300 °C. The structure, surface composition and both, optical and electrical properties of the layers were investigated. Optical parameters were characterized by spectrophotometry and ellipsometry, atomic force microscopy (AFM), scanning electron microscopy (SEM) and four-pointed probe as well as X-ray diffraction (XRD). In order to measure the resistivity of the connection zone between electrode and deposit layer transmission line method (TLM) was used. The connection zone between electrode and ITO layer were manufactured in the temperature range of 150-250 °C. Electrodes were formed from silver conductive paste. The use of ITO layer allows optimization of optical parameters in relation to electrical properties of the layer and enables creation of contacts with low resistivity values in low-temperature metallization processes.

1. Introduction
The ITO (Indium Tin Oxide) is commonly known as n-type Transparent Conductive Oxide (TCO) with the band gap energy varying from 3.0 to even 4 eV [1-2]. The ITO is often used in organic electroluminescence devices (for instance, organic light emitting diode (OLED) and thin-film transparent electrodes of liquid crystal displays (LCDs) [3, 4]. The high transparency of 85-90%, conductivity above 1000 S/cm, charge carrier density of 1·10^{21} carriers/cm^3 and mobility of 10-100 cm^2/Vs are the beneficial properties of ITO presented in the literature. The commercially available ITO targets with different doping content can be used for the ITO deposition at relatively low temperatures [5]. Few papers report on the effect of deposition temperature (between 150 °C and 180 °C) and annealing on changes of crystalline structure [6-8]. For example, paper [7] suggests that annealing temperatures above 250 °C are required in order to transform the amorphous ITO structure into the polycrystalline state. Various deposition methods have been used to deposit ITO such as evaporation, sputtering or sol-gel. [9]. The implementation of the paper achievements is in line with the key guidelines for the development of photovoltaics in the coming decade as a result of the possibility
of receiving contacts in low-temperature processes for the cells based on the construction of heterostructures, the application of low temperature metallization processes and the development of guidelines for metallization processes of conductive oxide layers applied by magnetron sputtering technique [10-14].

The aim of the work was to manufacture a layer with an admixture gradient, since it combines two important properties as the high transparency at visible wavelengths and the satisfactory electrical conductivity especially directly under the electrical contact. It is the main point of innovation of obtaining the proposed layer based on its possible bifunctional properties. The application of the mentioned layer is dedicated to the heterojunction solar cells production.

2. Material for investigation
The investigations were carried out on two inches polished monocrystalline silicon wafers (Cz-Si), p-type conductivity, 380 µm ± 25 µm thick, resistivity 7.5 ÷ 8 Ω·cm and (100) orientation of the crystallographic surface. The boron-silicon optical slides 30 mm x 30 mm and 1 mm thick were used for the experiments together with two ITO discs; In$_2$O$_3$ and SnO$_2$ both of 99.99% purity and suitable for producing layers of mixed indium tin oxide (ITO) with resistivity depending on composition.

2.1. Preparation of investigated samples
Silicon wafers were chemically cleaned with a standard procedure based on HCl and HF solutions. Optical glasses were washed in an ultrasonic bath.

2.2. Choice of parameters
The deposition of the In$_2$O$_3$, SnO$_2$ and ITO layers on the prepared substrates was performed by the magnetron sputtering method in the Institute of Catalysis and Surface Chemistry (figure 1).

![Figure 1. Test stand: a) device for applying layers by magnetron sputtering containing plasma pre-cleaning chamber and deposition chamber containing classic disk magnetron, b) In$_2$O$_3$ disk mounted, c) Si wafer before applying the layer, d) Si plate after depositing the layer.](image)

3. Research methodology
The following investigations were performed:

- the selection of parameters of the layer deposition process by the magnetron sputtering method with the application of a device produced by company MeasLine Sp, zoo. The samples were kept at room temperature during the deposition. An alternating current (AC) of magnetron mode was used with the frequency of 40 kHz. The magnetron diameter was 2". The deposition was carried out under Ar inflow to the pressure of $3 \cdot 10^{-3}$ mbar at base vacuum $5 \cdot 10^{-6}$ mbar. The growth rate was controlled by using a quartz microbalance. During the deposition process the following parameters were applied: deposited thickness from 30 to 170 nm and power of magnetron 100 W.

- the measurement of optical properties of the investigated samples, including reflection and transmission coefficient using a UV-VIS-NIR Lambda 950S spectrophotometer;

- the analysis of the chemical and phase composition of the structures investigated using scattered X-ray energy spectroscopy (EDS) and X-ray diffraction with a D8 Discover diffractometer.
produced by Bruker Company, a cobalt lamp with the wavelength of 1.78896 Å measured in Theta/2Theta geometry.

- the doping distribution in thin films was characterized using the secondary ion mass spectrometry (SIMS) technique on a CAMECA IMS6F system performed with cesium (Cs+) primary beam, at the energy of 14.5 keV with the current kept at 20 nA. The size of the raster was about 200x200 microns and the secondary ions were collected from the central region of 60 microns in diameter. Secondary ions OCs+, SiCs+, SnCs+, and InCs+ signals were collected. The use of Cs+ primary ions along with the detection of MCs+ molecular clusters (where M is the element to be monitored) in SIMS depth profiling was shown to be an efficient method of minimizing the variations of ion yields with sample composition.

- the surface topography of manufactured layers on monocrystalline silicon wafers investigation by using following methods: scanning electron microscopy; atomic force microscopy. The observation of the surface morphology of the investigated samples and the roughness measurement were performed under an atomic force microscope Park Systems XE 100 using intermittent contact mode;

- the measurement of sheet resistance of a silicon wafer with a four-pointed probe;

- measuring the conductivity type (p or n) using a hot probe;

- measuring the specific contact resistance $\rho_c$ of the front contact solar cell using the Transmission Line Model method (TLM) on the measuring position [13] including the size of the front electrode strips for 0.2×8 mm system distances between them: 2.5, 5 and 10 mm. TLM consisted in direct current (I) measurement and voltage (U) measurement between any two separate contacts. The electrodes were made of low-temperature silver conductive ink. The front contact paste was applied by screen printing method using a template.

- The thickness of thin layers measured with the Sentech SE 800PV spectral ellipsometer.

4. Results and discussion

Figure 2 presents the results of the transmission coefficient measurement in the range of 250 – 1200 nm conducted for the chosen tin, indium and indium-tin oxides. The transmission plots for all layer thicknesses is not shown because as expected its value decreased with the increase of the layer thickness. Instead, only the curves for the thickest ITO, SnO$_2$ and In$_2$O$_3$ layers were collected. The selected results (figure 2) roughly represent the optical properties of the produced materials.

The transmission curve for ITO and In$_2$O$_3$ are very similar. This is the first signal that there is a smaller share of SnO$_2$ than In$_2$O$_3$ in the produced ITO. The minimum transmission is located at 302 nm for ITO, 308 nm for In$_2$O$_3$ and 315 nm for SnO$_2$. The maximum transmission, which is 90%, corresponds to 582 nm, 622 nm and 770 nm wavelength for ITO, In$_2$O$_3$ and SnO$_2$, respectively.

The band gap energy was determined by Tauc plot method in which the absorption coefficient is calculated from formula [15]:

$$\alpha=-(\ln(T/(1-R))/d$$

The calculation revealed the band gap energy to be 3.75 eV for SnO$_2$, 3.9 eV for In$_2$O$_3$ and 4.0 eV for ITO (figure 3) which corresponded to literature reports [16-18]. The results confirmed that the chemical composition of the produced layers was different, because it corresponded to the reference glass on which layers were deposited.
Figure 2. Transmission spectra of In$_2$O$_3$, SnO$_2$, ITO layers.

Figure 3. Band gap energy of In$_2$O$_3$, SnO$_2$ and ITO layers.

The XRD diffractograms obtained using the Bragg-Brentano test (figure 4) revealed the presence of very intensive peaks at 82 and 73° coming from the (100) Si substrate and less intense ones at 41 and 35°, which confirmed the presence of the ITO phase in the form of In$_{0.8}$Sn$_{0.2}$O$_3$ of composition to 56% In, 29% O and 15% Sn by weight.

As for the SIMS results, taking into account the InCs+/SnCs+ signals ratio, the ratio of In and Sn in InSnO was calculated to be 70/1 (figure 5). The SIMS study confirmed the distribution of elements in the layer, with In decreasing and Sn growing. Since the signal from indium is two orders of magnitude stronger than that from tin, considering that the masses of both are similar, it can be concluded that the major component of the produced ITO was In$_2$O$_3$.

Figure 6 shows the topography of the applied layers. Based on AFM images, it was found that the layers are characterized by a fine crystalline structure. In the case of In$_2$O$_3$ the surface roughness coefficient was in the range from 0.1 to 1.5 nm, while it was 0.1 nm for SnO$_2$ and from 0.2 to 1 nm for ITO (figure 7). Such an ITO roughness distribution may also indicate a higher content of In$_2$O$_3$. It is worth noting that the commercial ITO offered by Ossila has the roughness of 1.8 nm at about 100 nm thick layer.
Figure 4. X-ray diffraction pattern of ITO deposited layers using Bragg – Brentano technique (chosen sample).

Figure 5. SIMS of the ITO/Si interface layer at deposited thickness (a) 32.8 nm and (b) 53.85 nm.

Figure 6. Topography of the applied ITO layers with thickness (a) 142.60 nm (b) and 32.8 nm (chosen example) (AFM).

The type of conductivity of the investigated coatings was measured using a hot probe. The results confirmed that all layers were n-type semiconductors.
The effect of sputtering deposition on the electrical resistivity of the deposited layers (ITO and In$_2$O$_3$) was measured by the Transmission Line Model (TLM) method. The measured resistivity was calculated using formulas according to those given in [13]. Based on the TLM method, it was found that the smallest specific contact resistance was obtained in the third and fourth series of the investigated electrodes formed from silver paste (Figure 8). The minimum value of this specific contact resistance was equal 0.80 Ω·cm$^2$ for solar cells. These experiments confirmed the repeatability of the method used for the layer with the thickness of 32.8 nm.

![Figure 7. Results of roughness measurement for tested samples.](image)

**Table 1. Results of measured $R_s$ for investigated layers (chosen samples)**

| Deposited layer | No. | Measured thickness [nm] | $R_s$ [Ω/□] | $\rho$ [Ω·cm] |
|-----------------|-----|-------------------------|--------------|---------------|
| ITO             | 1   | 32.8                    | 313.58       | 10.29·10$^{-4}$|
|                 | 2   | 53.85                   | 168.54       | 9.08·10$^{-4}$|
|                 | 3   | 103.15                  | 139.53       | 14.39·10$^{-4}$|
|                 | 4   | 142.60                  | 90.96        | 12.97·10$^{-4}$|

Where: *sample measured using spectral ellipsometer

The effect of sputtering deposition on the electrical resistivity of the deposited layers (ITO, In$_2$O$_3$) was measured by the Transmission Line Model method. The measured resistivity can be calculated using formulas given in [13]. Based on TLM method, it was found that the smallest specific contact resistance is obtained in the third and fourth series of investigated electrodes formed from silver paste (Fig. 8). The minimum value of this specific contact resistance is equal 0.80 Ω·cm$^2$ for solar cells. These studies confirmed the repeatability of the method used for the layer with the thickness of 32.8 nm.

![Figure 8. Specific contact resistance of In$_2$O$_3$ (a) and ITO (b) layers deposited at various thicknesses](image)

The observations in the scanning electron microscopy let establishing that the morphology of contacts deposited with the applied paste and dried in the dryer (time 5 minutes and temperature 130 °C) shows...
a very porous structure, which is a consequence of contact pitting and melting. Its thickness is contained in the range of 1 to 2 mm. Moreover, the obtained contacts demonstrate the structure with similar density grades, which often depend on drying temperature. The exemplary morphology of the contact produced by a pen with template is shown in figure 9. The layer was well sintered ensuring a good contact. Based on the SEM observations it was found that contacts obtained with applied paste demonstrated the connection with layer without defects and delaminations. Moreover, these contacts demonstrated porous structure similar to those obtained as a result of co-firing with the standard PV 145 paste and their porosity grade depended on co-firing temperature, similarly to the case of the commercial paste.

Figure 9. Exemplary surface layer topography obtained using silver paste on ITO_32.8 nm surface at different magnifications.

5. Conclusions

Indium, tin and indium-tin oxides of various thicknesses were deposited on silicon substrates using the magnetron sputtering method. The produced layers were characterized by a fine crystalline structure and small roughness. The transmission coefficients for the In$_2$O$_3$ and ITO layers were similar, while for SnO$_2$ the absorption edge shifted towards longer wavelengths. Also, the maximum transmission peak (90%) for SnO$_2$ (770 nm) was shifted compared with ITO (582 nm) and In$_2$O$_3$ (622 nm). The band gap energy was determined with the Tauc plot technique and it was equal 3.75 eV, 3.9 eV and 4.0 eV for SnO$_2$, In$_2$O$_3$ and for ITO, respectively, which corresponds with the literature data. The analysis of the dopant distribution with the SIMS method indicated a greater share of indium than tin in the obtained ITO layer. The XRD study confirmed that the composition of the ITO is In$_{0.8}$Sn$_{0.2}$O$_3$. The sheet resistance measurement revealed that the thinnest layers had the best electrical properties. The lowest specific resistance value measured by the TLM method was obtained for the ITO layer. The results confirmed that the electrical and optical properties of the investigated layers depended on the applied admixture gradient.

Acknowledgements This research was founded by Grant Number DEC-2018/02/X/ST8/01004.

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