BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. 69(6), 2021, Article number: e139005
DOI: 10.24425/bpasts.2021.139005

Optimised magnetron sputtering method for the deposition of indium tin oxide layers

Małgorzata MUSZTYFAGA-STASZUK[1*], Dušan PUDIŠ[2], Robert SOCHA[3], Katarzyna GAWLIŃSKA-NĘCEK[4], and Piotr PANEK[4]

[1] Silesian University of Technology, Welding Department, ul. Konarskiego 18A, 44-100 Gliwice, Poland
[2] Faculty of Faculty of Electrical Engineering and Information Technology, Department of Physics, Zilina, Slovakia
[3] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland
[4] Institute of Metallurgy and Materials Science PAS, ul. Reymonta 25, 30-059 Krakow, Poland

Abstract. The article presents the method of magnetron sputtering for the deposition of conductive emitter coatings in semiconductor structures. The layers were applied to a silicon substrate. For optical investigations, borosilicate glasses were used. The obtained layers were subjected to both optical and electrical characterisation, as well as structural investigations. The layers on silicon substrates were tested with the four-point probe to find the dependence of resistivity on the layer thickness. The analysis of the elemental composition of the layer was conducted using a scanning electron microscope equipped with an EDS system. The morphology of the layers was examined with the atomic force microscope (AFM) of the scanning electron microscope (SEM) and the structures with the use of X-ray diffraction (XRD). The thickness of the manufactured layers was estimated by ellipsometry. The composition was controlled by selecting the target and the conditions of the application, i.e. the composition of the plasma atmosphere and the power of the magnetrons. Based on the obtained results, this article aims to investigate the influence of the manufacturing method and the selected process parameter on the optical properties of thin films, which should be characterised by the highest possible value of the transmission coefficient (>85–90%) and high electrical conductivity.

Key words: In_2O_3; Sn_2O; ITO; magnetron sputtering method.

1. INTRODUCTION

The structure and properties of the surface layers mainly determine the functional properties of many products. Due to their application, the surface layers can be divided into those that exhibit the required physical properties that ensure the specific anti-corrosive mechanical properties of the products, including those of an anodic or cathodic nature and anti-electrochemical corrosion. They can also be divided into decorative and protective ones, which ensure the products have an external aesthetic appearance and resist corrosion [1, 2].

Transparent conductive oxides (TCOs) have attracted broad interest and are extensively used as low emissivity layers in architectural glass or as transparent electrodes in multiple devices (for photovoltaic solar cells and instance electrochromic devices) or more advanced electronic systems [3–6]. Such transmission layers are most often obtained based on indium, tin, and zinc compounds doped with tin (IV). This is the case for a matrix of In_2O_3, In_2O_3, or SnO_2 [7, 8]. The dopant fraction typically does not exceed 10% [8].

The lowest resistances are obtained for indium oxide layers doped with oxide tin, and they are the most common; because of the high price of indium, the search for cheaper and equally effective substitutes is of great importance. As a conductive oxide material, tin (IV) oxide is widely used for the fabrication of thin films because of its beneficial properties like high mechanical, chemical, environmental resistance, stability, and low cost [8]. SnO_2 is a semiconductor whose properties are determined by a wide bandgap (3.5–4 eV) [9]. In practical solutions, tin (IV) oxide is used in a form doped with fluorine or antimony since it conducts poorly [10]. Indium-tin oxide (ITO) belongs to electronically conductive transparent layers. ITO, commonly known in the literature [11, 12], is characterised by a heavily doped and highly degenerated n-type semiconductor with a high carrier concentration $\left(\sim 10^{21}\ \text{cm}^3\right)$. Because of its unique combination of excellent electrical conductivity and optical transparency, relatively good chemical stability, and good mechanical properties, it is one of the most widely used transparent conductive oxides [13–15]. For example, it has been shown in [15] that ITO thin films could reach high transparency in the visible region (90%) and high conduction properties $(\rho = 2\times 10^{-4}\ \Omega\cdot\text{cm})$. Results obtained in the works mentioned above the required high substrate temperatures during the deposition or the post-annealing process afterwards. That was so because of the main conduction mechanisms in ITO layers in which a high temperature promotes crystallisation of the layers and the creation of the oxygen vacancy [15]. Some of those papers have shown process parameters and optoelectronic properties for high-temperature ITO layers [16, 17]. Nowadays, it is still a challenge at an industrial scale to manufacture ITO films

*e-mail: malgorzata.musztyfaga@polsl.pl

Manuscript submitted 2021-06-09, revised 2021-09-01, initially accepted for publication 2021-09-27, published in December 2021

© 2021 The Author(s). This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

of competitively high quality at room temperature [18, 19]. The most suitable technology fulfilling these requirements is the magnetron sputtering technology [20]. Layer deposition by reactive magnetron sputtering has many advantages, such as uniform thickness, high mechanical strength, good adhesion to the substrate, easy-to-control structure, and composition of the coating [21]. This method can be applied to a wide variety of materials and is easily scalable. Several thin films (for example, Cu_2O and TiO_2) and structures (for example, TiO_2/Cu_2O) were fabricated by this technology [22]. Magnetron sputtering has become a critical deposition technology for thin films in many industrial applications in recent years. These include, but are not limited to, metallisation of integrated circuits, wear-resistant coatings, and corrosion protection, and much more [23]. In order to manufacture copper oxides, other methods can be applied such as sol-gel, evaporation, and sputtering [24].

This article aims to produce and investigate the ITO layers in terms of their influence on optical and electrical parameters.

2. MATERIAL FOR RESEARCH AND METHODOLOGY

2.1. Material for research

In the experiment, the thin In_2O_3, SnO_2, and ITO layers were deposited by the Magnetron Sputtering method. The coatings were deposited on both p-type Cz-Si wafers (380 μm ± 25 μm thick, resistivity 7.5–8 Ωcm and (100) orientation) and borosilicate glasses (30×30 mm with 1 mm of thickness), and two targets (In and Sn alloy type, 99.99% purity and 99:10 (wt.%) alloy composition). Before deposition, silicon wafers were chemically etched, while optical glasses were cleaned in the ultrasonic bath.

2.2. Methodology

The following investigations were performed in this paper:

1. Selection of magnetron sputtering parameters using a device produced by the company MeasLine Sp. z o.o. An alternating current (AC) of magnetron mode was used with a frequency of 40 kHz. The magnetron diameter was 2". The deposition was carried out in the Ar atmosphere with gas pressure 3×10^{-3} mbar. The samples were kept at room temperature.
2. Measurement of sheet resistance of a silicon wafer with a four-pointed probe.
3. Measurement of the conductivity type (p or n) using a hot probe.
4. The thickness of thin layers estimation with the Sentech SE 800PV spectral ellipsometer.
5. Optical properties measurement (for example reflection, transmission coefficient) by using UV-VIS-NIR Lambda 950S spectrophotometer.
6. Topography of the deposited layers analysis by the atomic force microscope (Park Systems XE 100) in the non-contact mode and Zeiss Supra 35 scanning electron microscope (SEM).
7. Analysis of the phase composition of the investigated structures using 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.
8. The thickness of manufactured metallisation was observed using a Zeiss confocal laser scanning microscope 5 (CLSM). The profile of thickness contact was determined based on three medium measurements.
9. Measurement of the work of the electron output from the Fermi level to the vacuum. The contact potential difference (CPD) is measured in relation to the output work (PE) for gold of 4.815 eV.

3. SELECTION OF PARAMETERS

The parameters for the application of the investigated layers (i.e. In_2O_3, SnO_2, ITO) on the prepared substrates were selected in a device provided by the Institute of Catalysis and Physiochemistry of the Polish Academy of Sciences in Krakow (Fig. 1). The thickness of the applied layers was also changed (from 30 to 165 nm). The deposition rate was monitored with a quartz microbalance.

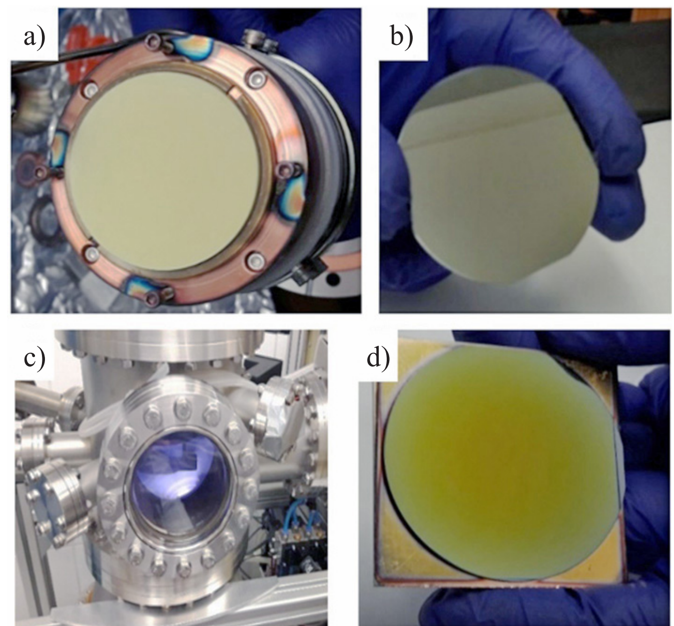


Fig. 1. Layer deposition stand using magnetron sputtering method: a) In_2O_3 disc mounted, b) silicon wafer before the process, c) magnetron sputtering chamber, d) silicon wafer with In_2O_3 layer after the process

4. RESULTS AND DISCUSSION

In the investigation, the two series of samples were prepared by the magnetron sputtering method (Table 1). This table shows the results of the electrical properties of the investigated layers. Based on the obtained conductivity test results, it was found that the investigated layers were n-type semiconductors. Resistivity calculation revealed that the lowest value of ρ was obtained for the thinnest cover for both In_2O_3 (12.68×10^{-4} Ωcm) and ITO (8.04×10^{-4} Ωcm). It should be noticed that either conductivity type or sheet resistance could not be measured for SnO_2, which indicates a very high layer resistivity.

TABLE 1

Material data and selected results of electrical properties (where: SnO_2 – is the insulator)

Series	I				II				III			
Sample	1	2	3	4	5	6	7	8	9	10	11	12
Substrate	Optical slide											
Type of deposited layer	In_2O_3				SnO_2				ITO			
Thickness measured *(nm)	34.1	65.61	96.56	146.56	34.13	63.47	99.03	157.79	30.1	63.85	98.15	162.6
Conductivity type (p/n)	n				–				n			
Sheet resistance – Rp (Ω/□)	372	250	231	152	–	–	–	–	267	166	125	96
Resistivity – ρ(Ωcm)	12.68×10^{-4}	16.40×10^{-4}	22.31×10^{-4}	22.28×10^{-4}	–	–	–	–	8.04×10^{-4}	10.62×10^{-4}	12.23×10^{-4}	15.60×10^{-4}

Figure 2 presents the results of the transmission coefficient measurement in the range of 250–800 nm for the chosen oxides. As was expected, the absorption edge shifts towards longer wavelengths (from 250 to 350 nm) with the layer thickness increase. This is especially evident for the In_2O_3 and SnO_2 layers. For ITO, the absorption edge insignificantly shifts and slightly deviates from the absorption edge of the glass substrate. On the other hand, the increase in the absorption of long wavelengths in the layer is visible with the increase in its thickness. The value of the absorption edge for the sample is equal: 2–270 nm, 3–300 nm, 4–310 nm; in the case of sample 1, it is difficult to read the edge of the absorption because the layer is very thin (Fig. 2a). The value of the absorption edge for the sample is equal: 2–270 nm, 3–300 nm, 4–310 nm (Fig. 2a). The value of the absorption edge for the sample is equal: 6–270 nm, 7–310 nm, 4–340 nm (Fig. 2b). In the case of samples 1 and 5, it is difficult to read the edge of the absorption because the layer is very thin. For the samples from 9 to 12, the absorption edge is equal to 300 nm.

The bandgap energy was determined by the Tauc plot method in which the absorption coefficient (α) is calculated from formula (1):

$$\alpha = -\left(\ln\left(T/(1-R)\right)/d\right), \tag{1}$$

where d – thickness of the tested layer, T – transmission coefficient at a given wavelength, R- reflection coefficient.

The calculation revealed that In_2O_3 and SnO_2 are 3.7 eV, while for ITO layers, the bandgap energy is from 3.9 eV (Fig. 3), which corresponded to the literature reports [25–27].

The topography of the deposited layers is presented in Fig. 4. Based on AFM images, it was found that a finely crystalline structure characterises the investigated layers. Based on the performed investigations in the atomic force microscope, it was found that in the case of samples with deposited In_2O_3 layers –the surface roughness coefficient ranges from 0.09 to 0.43 nm, samples with deposited SnO_2 layers – the surface roughness coefficient ranges from 0.1 to 0.14 nm, samples with deposited

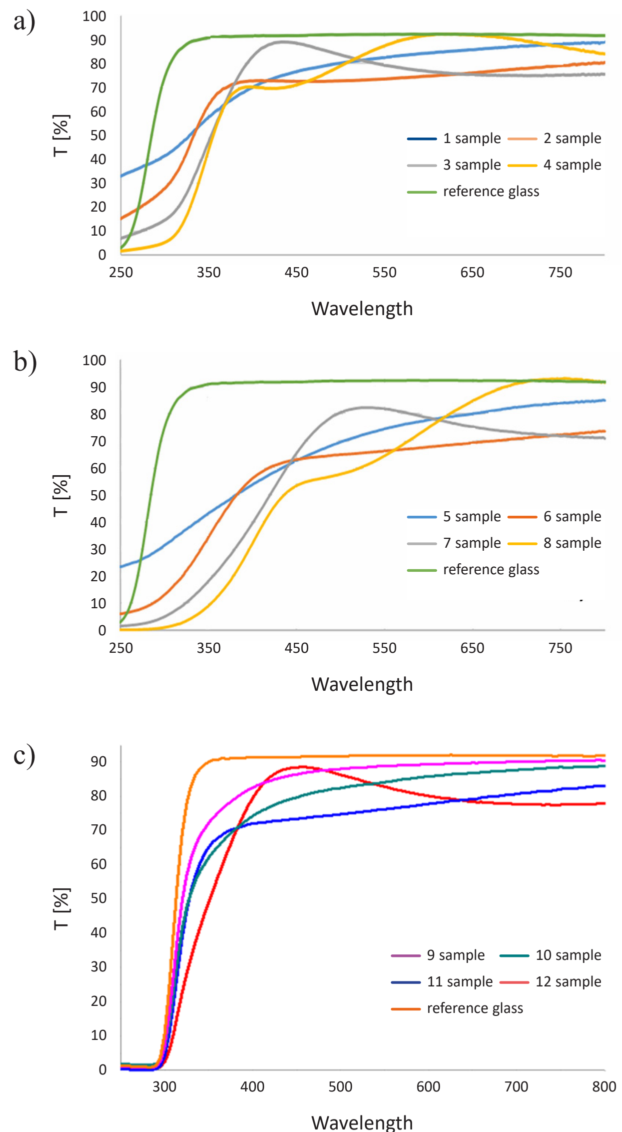


Fig. 2. Transmission spectra of the layer in the wavelength range 250 to 800 nm, where: a) In_2O_3, b) SnO_2, c) ITO

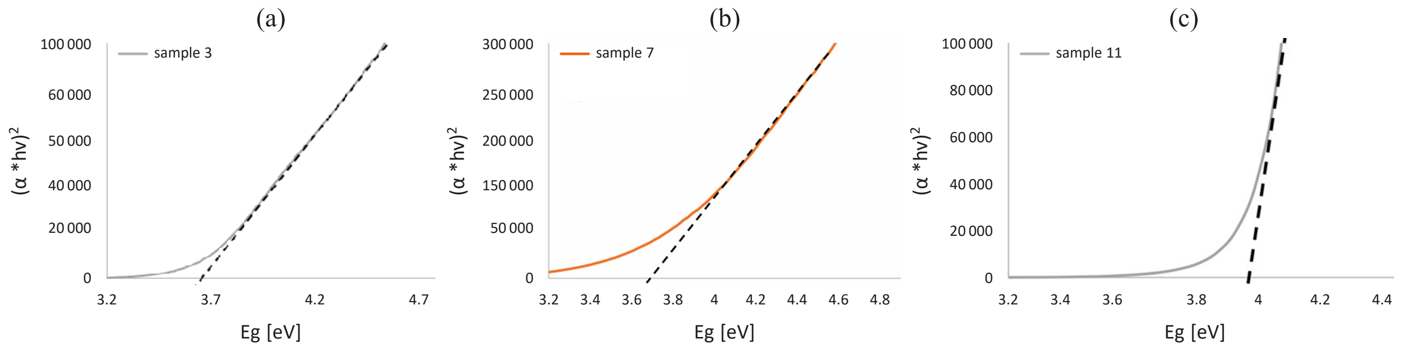


Fig. 3. Bandgap energy of a) In_2O_3, b) SnO_2, and c) ITO layers (chosen samples)

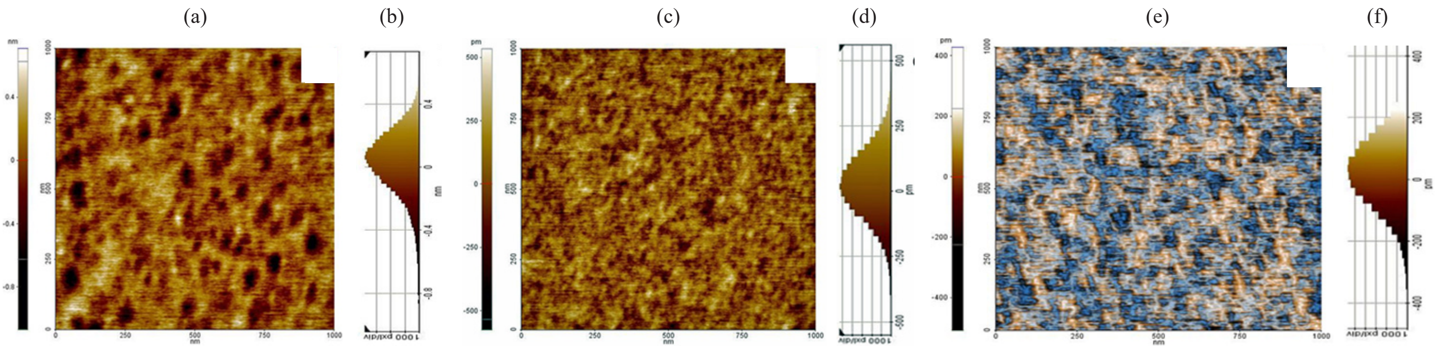


Fig. 4. 3D (a, c, e) AFM image and histogram; (b, d, f) for sample surfaces produced by a magnetron sputtering method (where: a-b – In_2O_3 layer – 65.61 nm, c-d – SnO_2 – 63.47 nm, e-f-ITO – 63.85 nm)

ITO layers – the surface roughness coefficient ranges from 0.09 to 0.13 nm.

EDS results confirmed proper elemental compositions of the produced oxides (Fig. 5). After the qualitative phase analysis by the X-ray diffraction method, it was confirmed that the ITO layer (Fig. 6) was obtained on silicon substrates as assumed. Besides, Si reflections from the substrate appear on the X-ray diffraction patterns made using the classic Bragg-Brentano technique (Fig. 6). The front contacts were deposited with silver conductive paste and dried for 6 minutes at 130°C. The observations in the scanning electron microscopy indicate that the morphology of investigated metallisation shows a porous structure with different grain sizes (Fig. 7).

The thickness of the front electrode was determined by checking the height profile of the three-dimensional surface topography measured using the confocal laser scanning microscope (Fig. 8). A medium thickness of the electrode is equal to 21 μm (Fig. 8).

The work function (Φ), the energy difference between Fermi level and vacuum, was determined for the manufactured layers

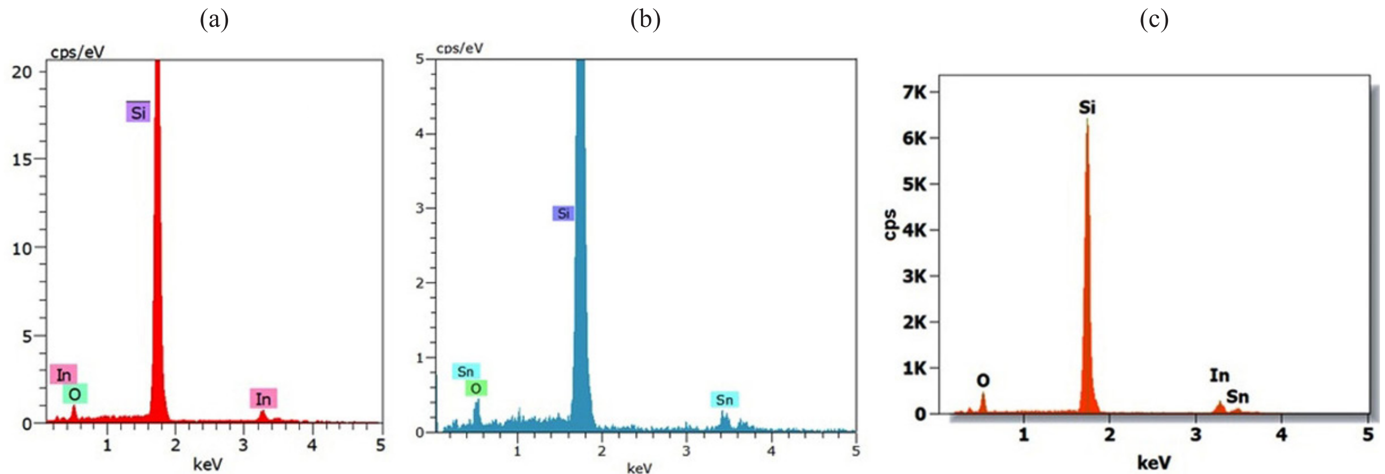


Fig. 5. Analysis of the chemical composition by the EDS method from the micro area of a) In_2O_3; b) SnO_2, ITO layers (SEM)

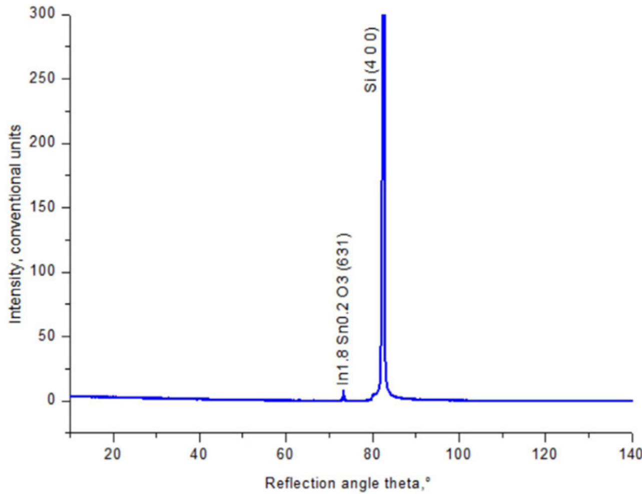


Fig. 6. X-ray diffraction pattern of the ITO deposited layer on a silicon substrate using Bragg – Brentano technique (chosen sample)

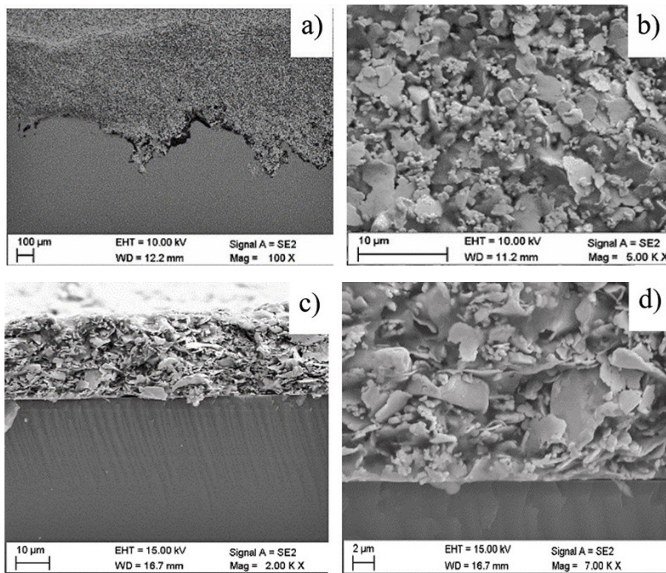


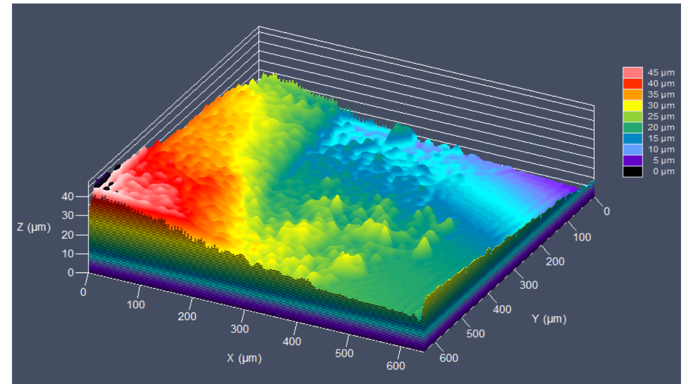
Fig. 7. SEM images of the topography (a, b) and cross-section (c, d) of the front electrode deposited on the ITO surface

(Table 2). Based on the obtained results, it was found that the lowest value of the work function is 4.463 eV for SnO_2.

TABLE 2

Work function calculated after the determination of the contact potential difference compared to the literature data

Selected layers	The work function for selected layers (eV)	The measured contact potential difference (mV)	The work function for selected layers (eV) found in the literature
ITO	4.598	–217.5	4.80 [28]
In_2O_3	4.625	–190.2	3.75 [29]
SnO_2	4.463	–352.6	3.75 [29]



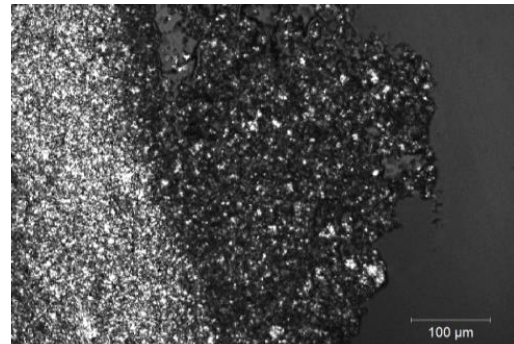


Fig. 8. Three- and two-dimensional surface topography (CLSM) of front electrode obtained from conductive paste deposited on the ITO (30.1 nm) surface (example)

5. SUMMARY

The investigated ITO thin layers were prepared by magnetron sputtering technique. Studies have shown that the influence of applied technique and layer thickness on the analysed properties is significant. The bandgap energy was determined with the Tauc plot technique, and it was equal to 3.7 eV for SnO_2 and In_2O_3. In the case of ITO, the bandgap energy was 3.9 eV. The proposed method of thin-layer production facilitates obtaining a material with a fine crystalline structure and small roughness. It should be highlighted that the roughness was obtained for the thinnest layers, which were also characterised by the lowest resistivity.

ACKNOWLEDGEMENT

The article was published as part of a scholarship awarded by the International Visegrad Foundation for the submitted project number 520110061 by Eng. M. Musztyfaga-Staszuk, PhD, DSc.

REFERENCES

[1] L. Żukowska, J. Mikuła, M. Staszuk, and M. Musztyfaga-Staszuk, "Structure And Properties Of PVD Coatings Deposited On Cermets," *Arch. Metall. Mater.*, vol. 60, no. 2, pp. 727–733, 2015, doi: 10.1515/amm-2015-0198.

[2] M. Staszuk *et al.*, "Investigations of TiO_2, Ti/TiO_2, and $Ti/TiO_2/Ti/TiO_2$ coatings produced by ALD and PVD methods on Mg-(Li)-Al-RE alloys substrates," *Bull. Pol. Acad. Sci. Tech. Sci.*, vol. 69, no. 5, p. 137549, 2021 (in print), doi: 10.24425/bpasts.2021.137549.

[3] Y.-S. Cho, M. Han, and S. H. Woo, "Electrospinning of Antimony Doped Tin Oxide Nanoparticle Dispersion for Transparent and Conductive Films," *Arch. Metall. Mater.*, vol. 65, no. 4, pp. 1345–1350, 2020, doi: 10.24425/amm.2020.133697.

[4] R.A. Maniyara, V.K. Mkhitaryan, T.L. Chen, D.S. Ghosh, and V. Pruneri, "An antireflection transparent conductor with ultralow optical loss (<2%) and electrical resistance," *Nat. Commun.*, vol. 7, pp. 13771, 2016, doi: 10.1038/ncomms13771.

[5] M. Kuc *et al.*, " ITO layer as an optical confinement for nitride edge-emitting lasers," *Bull. Pol. Acad. Sci. Tech. Sci.*, vol. 68, no. 1, 2020, doi: 10.24425/bpasts.2020.131834.

[6] Y. Cui and C.M. Lieber, "Functional Nanoscale Electronic Devices Assembled Using Silicon Nanowire Building Blocks," *Science*, vol. 291, pp. 851–853, 2001, doi: 10.1126/science.291.5505.851.

[7] J. Kryłow, J. Oleński, Z. Sawicki, and A. Tumański, "Doping of semiconductors, Technological processes in semiconductor electronics," Scientific and Technical Publishing House, Warsaw 1980 [in Polish].

[8] Ş. Ţălu, S. Kulesza, M. Bramowicz, K. Stępień and D. Dastan, "Analysis of the Surface Microtexture of Sputtered Indium Tin Oxide Thin Films," *Arch. Metall. Mater.*, vol. 66, no. 2, pp. 443–450, 2021, doi: 10.24425/amm.2021.135877.

[9] Y.S. Hsu and S.K. Gandhi, "The Effect of Phosphorus Doping on Tin Oxide Films Made by the Oxidation of Phosphine and Tetramethyltin II. Electrical Properties J. Electrochem. Soc. II," *Sol. State Sci. Technol.*, vol. 127, p. 1592, 1980.

[10] T. Nakahara and H. Koda, *Chemical Sensor Technology*. Ed., N. Emazoe," Elsevier, New York, 1991, vol. 3, p. 19.

[11] S.-J. Hong, S.-H. Song, B.J. Kim, J.-Y. Lee, and Y.-S Kim, "ITO Nanoparticles Reused from ITO Scraps and Their Applications to Sputtering Target for Transparent Conductive Electrode Layer," *Nano Converg*., vol. 4, no 23, p. 23, 2017.

[12] Q. Li, E. Gao, and A.X. Wang, "Ultra-Compact and Broadband Electro-Absorption Modulator Using an Epsilon-near-Zero Conductive Oxide," *Photonics Res.*, vol. 6, no. 4, pp. 277–281, 2018, doi: 10.1364/PRJ.6.000277.

[13] K. Ellmer, "Past Achievements and Future Challenges in the Development of Optically Transparent Electrodes," *Nat. Photonics*, vol. 6, pp. 809–817, 2012, doi: 10.1038/nphoton.2012.282.

[14] Q. Li *et al.*, "3D ITO-Nanowire Networks as Transparent Electrode for All-Terrain Substrate," *Sci. Rep.*, vol. 9, no. 4983, 2019.

[15] C. Guillén and J. Herrero, "Comparison study of ITO thin films deposited by sputtering at room temperature onto polymer and glass substrates," *Thin Solid Films*, 480–481, pp. 129–132, 2005, doi: 10.1016/j.tsf.2004.11.040.

[16] C. Guillén and J. Herrero, "Polycrystalline growth and recrystallisation process in sputtering ITO thin films," *Thin Solid Films*, vol. 510, pp. 260–264, 2006.

[17] H. Morikawa and M. Fujita, "Crystallisation and electrical property change on the annealing of amorphous indium-oxide and indium tin oxide films," *Thin Solid Films*, vol. 359, pp. 61–67, 2000.

[18] F. Kurdesau, G. Khripunov, A.F da Cunha, M Kaelin, and A.N Tiwari, "Comparative study of ITO layers deposited by DC and RF magnetron sputtering at room temperature," *J. Non-Crystall. Solids*, vol. 352, pp. 1466–1470, 2006, doi: 10.1016/j.jnoncrysol.2005.11.088.

[19] C.L. Tien, H.Y. Lin, C.K. Chang, and C.J. Tang, "Effect of Oxygen Flow Rate on the Optical, Electrical, and Mechanical Properties of DC Sputtering ITO Thin Films," *Adv. Condens. Matter Phys.*, 2019, p. 2647282, 2019.

[20] J. Txintxurreta, E. G-Berasategui, R. Ortiz, O. Hernández, L. Mendizábal, and J. Barriga, "Indium Tin Oxide Thin Film Deposition by Magnetron Sputtering at Room Temperature for the Manufacturing of Efficient Transparent Heaters," *Coatings*, vol. 11, p. 92, 2021, doi: 10.3390/coatings11010092.

[21] R.K. Tyagi, P. Saxena, A. Vashisth, and S. Mehndiratta, "PVD based thin film deposition methods and characterisation/ property of different compositional coatings- a critical analysis," *Materials Today: Proceedings 2nd International Conference*, vol. 38, pp. 259–264, 2020.

[22] P. Sawicka-Chudy *et al.*, "Characteristics of TiO_2, Cu_2O, and TiO_2/Cu_2O thin films for application in PV devices, *AIP Advances*, vol. 9, p. 055206, 2019, doi: 10.1063/1.5093037.

[23] B. Wicher *et al.*, "Structure and Electrical Resistivity Dependence of Molybdenum Thin Films Deposited by DC Modulated Pulsed Magnetron Sputtering," *Arch. Metall. Mater.*, vol. 63, no. 3, pp. 1339–1344, 2018, doi: 10.24425/123809.

[24] L.J. Meng, E. Liang, J. Gao, V. Teixeira, and M.P. dos Santos, "Study of indium tin oxide thin films deposited on acrylics substrates by ion beam assisted deposition technique," *J. Nanosci. Nanotechnol.*, vol. 9, pp. 4151–4155, 2009, doi: 10.1166/jnn.2009.m24.

[25] J.C. Manifacier, M. De Murcia, J.P. Fillard, and E. Vicario, "Optical and electrical properties of SnO_2 thin films in relation to their stoichiometric deviation and their crystalline structure," *Thin Solid Films*, vol. 41, pp. 127–144, 1977.

[26] M. Iftikhar, I.M. Ali, and M.A. Al-Jenabi, "Structural and Optical Properties of In_2O_3 and Indium Tin Oxide Thin Films," *J. Unive. Anbar Pure Sci.*, vol. 11, no.1, pp. 39–46, 2017.

[27] H. Kim *et al.*, "Electrical, optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices," *J. Appl. Phys.*, vol. 86, pp. 6451–6461, 1999, doi: 10.1063/1.371708.

[28] N. Nosidlak, "Application of polymer systems as materials in photovoltaic cells and electroluminescent diodes". PhD Thesis, Krakow 2013.

[29] L.F.J. Piper *et al.*, "In_2O_3 is found about 2.8 eV below the Fermi level," *Appl. Phys. Lett.*, vol. 94, p. 022105, 2009.