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

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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: In2O3; SnO2; 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 In2O3, In2O3, or SnO2 [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]. SnO2 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 (~1021 cm−3). 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 (ρ = 2×10−4 Ω·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...
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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 of 40 mbar. The samples were kept at room temperature.


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$_2$O$_3$, 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.

2. MATERIAL FOR RESEARCH AND METHODOLOGY

2.1. Material for research

In the experiment, the thin In$_2$O$_3$, 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 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.

Layer deposition stand using magnetron sputtering method: a) In$_2$O$_3$ disc mounted, b) silicon wafer before the process, c) magnetron sputtering chamber, d) silicon wafer with In$_2$O$_3$ layer after the process.

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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$_2$O$_3$ (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.
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Fig. 2. Transmission spectra of the layer in the wavelength range 250 to 800 nm, where: a) In$_2$O$_3$, b) SnO$_2$, c) ITO

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$_2$O$_3$ 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: 6‒270 nm, 7‒310 nm, 8‒340 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 ($\alpha$) is calculated from formula (1):

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

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

The calculation revealed that In$_2$O$_3$ 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$_2$O$_3$ 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 SnO$_2$ – is the insulator.

<table>
<thead>
<tr>
<th>Material data and selected results of electrical properties (where: SnO$_2$ – is the insulator)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series</strong></td>
</tr>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
</tr>
<tr>
<td><strong>Type of deposited layer</strong></td>
</tr>
<tr>
<td><strong>Thickness measured <em>(nm)</em></strong></td>
</tr>
<tr>
<td><strong>Conductivity type (p/n)</strong></td>
</tr>
<tr>
<td><strong>Sheet resistance – Rp (Ω/□)</strong></td>
</tr>
<tr>
<td><strong>Resistivity – ρ(Ωcm)</strong></td>
</tr>
</tbody>
</table>
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. 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 SnO₂.

TABLE 2

<table>
<thead>
<tr>
<th>Selected layers</th>
<th>The work function for selected layers (eV)</th>
<th>The measured contact potential difference (mV)</th>
<th>The work function for selected layers (eV) found in the literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>4.598</td>
<td>−217.5</td>
<td>4.80 [28]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>4.625</td>
<td>−190.2</td>
<td>3.75 [29]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>4.463</td>
<td>−352.6</td>
<td>3.75 [29]</td>
</tr>
</tbody>
</table>

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 SnO₂ and In₂O₃. 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. Muszyńska-Staszuk, PhD, DSc.

REFERENCES


