Practical Verification of ITO as a Transparent Emitter Electrode for Flexible Photovoltaic Structures

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Abstract
In this paper the mechanical, optical and electrical parameters of Indium Tin Oxide (ITO) Transparent Conductive Layers (TCL) are explored, analyzed and verified. Investigated Transparent Conductive Oxide (TCO) layers are deposited, using magnetron sputtering method, on flexible polymer PET foil, according to their photovoltaic (PV) cell emitter contact application. ITO-coated PET (polyethylene terephthalate) foils have been dynamically bent on numerous cylinders of various diameters according to the standard requirements. Sheet resistance per square, for each measured sample, are obtained and recorded during bending cycle. Thermal durability, as well as temperature influence on resistance and optical transmission are verified.

Moreover, numerical models of several thin-film photovoltaic cell structures, with ITO transparent conductive layers, are constructed. Computer simulations of basic and essential electrical and optical characteristics for selected solar cells are determined.

Presented results were conducted in order to verify practical suitability of Indium Tin Oxide as a front contact in flexible thin film photovoltaic cell structures.

1. Utilization of transparent electrodes in photovoltaic cells

An essential challenge in the development of flexible photovoltaic (PV) structures, excepting the elaboration of an appropriate semiconductor junction and optical properties of active layers, is providing suitable emitter contacts. PV electrodes are required to be reliable, efficient, low cost and compatible with solar cell structure.

1.1 Transparent Conductive Oxides (TCO)

An extremely frequently used solution is applying flexible Transparent Conductive Oxides (TCO) as PV cell front (generally emitter) layer electrodes. Emitter contacts are usually realized by using conductive transparent metal oxides, such as: SnO₂, ITO, ZnO₄, CdSnO₄, In₂O₃, ZnO:Al, as well as CdO, ZnO and RuSiO₄. In order to integrate solar cells into PV modules or for more convenient measurements execution, additional metal contacts attached to TCO are applied [1]. The most popular among listed TCO compounds is Indium Tin Oxide (ITO).

ITO is a mixture of tin (IV) oxide: SnO₂ and indium (III) oxide: In₂O₃. This material is characterized by high optical transmission of above 80% in visual range and relatively low electrical resistivity between 10÷100 Ω/square for thickness of 150 nm÷200 nm [2]. Unfortunately, applying ITO and other TCO layers, in flexible photovoltaic structures encounter several significant barriers. Both advantageous and disadvantageous characteristics were observed and are reported in this paper.

1.2 Transparent Conductive Layers (TCL)

An alternative method of creating flexible transparent contacts for photovoltaic devices is to use carbon compounds such as carbon nanotubes (CNT) or graphene. Due to the broad range of potential manufacturing techniques and diversified properties of such carbon compound layers, they are becoming increasingly popular in electronic applications [3]. Especially CNT or graphene layers, as well as their mixtures, obtained using low-cost techniques, such as screen printing, appear to be potentially intractable in this field. However, these research are still in the development stage. In Fig. 1 some exemplary experimental data of the optical transmission for three different TCLs (CNT, ITO and ZnO:Al) are shown.
Optical transmission is certainly dependent also on the thickness of deposited layer and predominantly proportional to the layer resistance. Therefore, the compromise between the highest transmission and the lowest resistance remains in the field of research.

2. Mechanical and thermal durability of Indium Tin Oxide on flexible substrate

Mechanical durability of the material and relative constancy of its sheet resistance value are very important factors if considered as a front transparent conductive coating of a flexible photovoltaic structure. In order to verify mechanical properties of Indium Tin Oxide, a set of samples was prepared and investigated.

Thin ITO layers were deposited on PET foil by magnetron sputtering method and afterwards substrate was cut into test samples of 1x15 cm dimensions to fit measuring system shown in Fig.2. Samples were subjected to dynamical bending, using specially constructed apparatus (Fig.2), on cylinders of six various diameters from 20 to 50 mm. For each sample (on each cylinder size) 200 bending cycles were performed (one cycle is one bent and straighten of the sample). Bending frequency was equal 3 cycles per second. Digital Rigol multimeter measured and recorder resistance values in the rate of 10 samples per second.

Moreover, average resistances of each sample were measured (and recalculated for resistance per square) in four different situations:

\[ R_0: \text{initial resistance}/\text{sq value – sample is plane;} \]
\[ R_1: \text{initial resistance}/\text{sq value – sample is statically bent on the cylinder;} \]
\[ R_2: \text{terminal resistance}/\text{sq value (after a series of bending cycles) – sample is statically bent on the cylinder;} \]
\[ R_3: \text{terminal resistance}/\text{sq value (after a series of bending cycles) – sample is plane;} \]

Results of above listed values (Tab.1 and Tab.2), as well as percentage changes of resistance per square during dynamic bending and resistance in time stabilization processes are shown below for two chosen cylinder diameters: 50 and 25 mm.

Particular graphs below (Fig.3 and Fig.5) present percentage variations of the resistance per square values of the sample during dynamical bending (on the cylinder of specified diameter), relatively to the resistance/sq of a plane sample, calculated from the formula (1):

\[ x = \frac{R_m - R_0}{R_0} \times 100\% \]  

where: \( R_0 \): initial resistance per square value of a plane sample, \( R_m \): measurement resistance per square (during bending).

Fig.4 and Fig.6 show the percentage changes of resistance per square during stabilization after dynamic bending, respectively for samples bent on 50 and 25 mm diameter cylinders. Given sample was left statically bent on the cylinder while the resistance stabilization process was in progress. The time of the procedure was 10 minutes.
from application in flexible photovoltaic structures. However, Fig.4 proves that measured layer resistance values start decreasing while dynamic bending stops (even though the sample is still statically bent on the cylinder). Moreover, when the sample is straightened again (after bending series), terminal value of R/sq is only 150% higher than the initial one (Tab.1). Nevertheless, there is still a great number, however if considered in terms of its initial resistance/sq value (42 Ohm/sq), it seems to be acceptable.

The situation is slightly different if bending angle is smaller. Results of R/sq values while bending was carried on 25 mm diameter cylinder are presented in Tab.2, Fig.5 and Fig.6.

<table>
<thead>
<tr>
<th>Tab.2. Resistance/sq for sample bent on 25mm cylinder.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0 ) [Ohm/sq]</td>
</tr>
<tr>
<td>41.34</td>
</tr>
</tbody>
</table>

Fig.5. Percentage changes of resistance per square during dynamic bending on 25mm cylinder (red line is an average value).

Fig.6. Percentage changes of resistance per square during stabilization after dynamic bending.

Fig.7. Temperature profile (programmed and actual) for the sample heated up to 150°C.

Results of resistance per square measured before and after heating up the sample are presented in Tab.3. Optical transmission of tested structures in the function of the light wavelength is demonstrated in Fig.8.

<table>
<thead>
<tr>
<th>Tab.3. Changes of resistance/sq after heating the sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
</tr>
<tr>
<td>R/sq [Ω/sq]</td>
</tr>
</tbody>
</table>

Fig.8. Optical transmission of ITO samples before and after heating.

Tab.3 and Fig.8 show that short-term exposure for the temperature lower or equal 150°C actually does not influence neither the resistance per square value, not optical transmission characteristic of ITO layer. Although, increasing treatment temperature up to 200°C causes significant changes especially in resistance value (Tab.3), which increases from 41 Ω/sq to 535 MΩ/sq. Optical transmission is reduced at about 1/3 of the reference spectrum. This huge resistance increase, as well as transmission deterioration, is caused not only by the ITO layer degradation, but also because of the substrate foil shrinkage (PET melting point is 260°C [4]).

However, previously conducted research [5], concerning long-term temperature tests, for ITO samples (deposited both on foil and glass), indicated the relationship between layer resistance and temperatures (100, 150 and 200°C), using standard programmable PEO 601 furnace. For this experiment, samples of ITO on PET foil of 5x5 cm dimensions were used. Exemplary heating profile, for the temperature of 150°C, is shown in Fig.7. Green curve represents programmed profile, yellow shows the actual temperature and red/blue line stands for the furnace power. Heating time was about 30 minutes.
temperature changes. Mentioned tests [5] were conducted in 130 thermal cycles of 1 hour each, within -40 to +125°C temperature range. Such examination was to simulate ageing processes which takes place in real atmospheric environment. Although, the measurements did not show the influence on layers optical transmission, they revealed 20% of the average resistance increase after the experiment, which is another disadvantage of examined material.

3. Performance of thin-film PV structures with ITO emitter contact layer

In order to investigate the performance of flexible thin film photovoltaic structures included ITO layers as front (emitter) transparent contacts, theoretical models were constructed. Computer simulations were conducted using specialized software dedicated for thin-film photovoltaic structures operation, called SCAPS (Solar Cell CAPacitance Simulator [6]). SCAPS is a one dimensional solar cell simulation program developed at the department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium. Because SCAPS is originally developed for PV cell structures of the CuInSe$_2$ (CIS) and the CdTe family and they are also potentially flexible structures, simulations were focused on two basic devices: CdTe and CIGS (Cu(In$_x$Ga$_{1-x}$)Se$_2$) based. Both further subchapters (3.1 and 3.2) present simulations in four different variants. The first one represents only photovoltaic structure where neither ITO layer parameters, nor contact shading were included (the most ideal option). The second variant still does not include ITO, but there is shading introduced by standard metal (Ag or Al) front emitter finger contacts. Shading was established at the level of 5% of the front surface of modeled solar cell. The last two variants involve ITO layers as transparent front electrodes. Obviously, this oxide coating is not perfectly transparent, therefore, instead of 5% shading of standard front contacts, ITO filters were inducted (filter values were calculated on the basis of experimental measurements of ITO layers on glass and PET foil). Shading by ITO filters was introduced in two options: one is pure ITO (without any substrate) and second represents ITO on PET foil.

3.1 CdTe based solar cells

Cadmium telluride based solar cells are among the most promising concepts in thin-film photovoltaics. With a bandgap of 1.45 eV it is well suited to match the AM 1.5 solar spectrum. Furthermore, its high absorption coefficient indicates that only a few micron thick absorber film is required for efficient solar cell operation [1]. General structure of the typical thin-film CdTe/CdS solar cell is shown in Fig.9 (left) as a cross section model in superstrate (reversed) configuration. It includes only a transparent conductive layer contact with no standard emitter fingers. Because of the specific reversed design, the substrate here is a front side. Fig.9 (right) represents SCAPS model of the structure.

![Fig. 9. Structure of CdTe thin film solar cell: left – cross section model [1], right – SCAPS model.](image)

In order to generate models of CdTe/CdS photovoltaic devices, in variants mentioned before, SCAPS built-in structure was used and modified (example CdTe.def model). In this model two CdTe layers are assumed: one next to the contact (3 μm) and the other next to the junction (6.9 μm) [6]. As a window layer thin (100 nm) CdS film is adopted.

Results of CdTe based solar cells simulations, in four previously described options, are presented below. The most important electrical parameters of modeled PV devices (V$_{oc}$: open circuit voltage, J$_{sc}$: short current density, FF: fill factor, Eff: efficiency) are collected in Tab.4. For proposed CdTe/CdS structures current-voltage characteristics (Fig.10) and quantum efficiency in the wavelength function (Fig.11) were obtained and compared.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>V$_{oc}$ [mV]</th>
<th>J$_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>no shading</td>
<td>753.74</td>
<td>21.66</td>
<td>45.00</td>
<td>7.35</td>
</tr>
<tr>
<td>5% shading</td>
<td>751.28</td>
<td>20.62</td>
<td>45.45</td>
<td>7.04</td>
</tr>
<tr>
<td>pure ITO</td>
<td>746.43</td>
<td>18.77</td>
<td>46.30</td>
<td>6.49</td>
</tr>
<tr>
<td>ITO on PET</td>
<td>744.65</td>
<td>18.07</td>
<td>46.61</td>
<td>6.27</td>
</tr>
</tbody>
</table>

![Fig. 10. Simulated J–V characteristics for CdTe based photovoltaic cell.](image)
Both Fig.10 and Fig.11 show the comparison of CdTe based photovoltaic structures in four variants. Red curves represent a configuration without ITO layer, where no front contact shading is included. Navy blue lines stand for the structure without ITO but including 5% shading derived from front metal contacts. Light green color characteristics simulate the operation of CdTe/CdS solar cell with ITO layer introduced as a front contact and optical transmission filter simulating shading by the ITO coating. Finally, pink curves correspond to the structure including ITO and its shading together with transparent PET foil.

Obtained simulation results suggest that the influence of transparent conductive ITO layer on CdTe based photovoltaic structure is not beneficial for its final performance. However, practical measurements on actual devices are needed to verify that.

### 3.2 CIGS photovoltaic structures

Another interesting material for thin-film solar cell absorber layer is copper indium diselenide CuInSe₂. CIS has a direct bandgap of 0.95 eV which can be increased by the addition of gallium to the absorber film. About 30% of Ga added to CIS layer (CIGS), changes the bandgap from 0.95 eV to almost 1.2 eV, which improves its match with the AM 1.5 solar spectrum. Higher gallium content (of 40%) has a detrimental effect on the device performance, because of its negative impact on the charge transport properties. The best gallium to indium ratio is 3:7 for high efficiency PV devices [1]. The typical thin-film CIGS photovoltaic structure consists respectively of: substrate (flexible or rigid), back metal contact, CIGS absorber layer, window layer (usually CdS) and transparent conductive layer. Fig.12 (left) presents an example CIGS cell structure manufactured in the Laboratory for Thin Films and Photovoltaics at EMPA, Switzerland [7]. Fig.12 (right) shows model applied in SCAPS simulator. Absorber Cu(In,Ga)Se₂ is defined as a p-type layer of 1 μm thickness and the bandgap of 1.1 eV. In the function of window layer CdS of 2.45 eV bandgap is assumed. Cadmium sulfide thickness in this modeled structure is 50 nm.

Analogically as in 3.1 subchapter, simulation results are presented in figures below (Fig.13: J-V characteristics, Fig.14: Quantum Efficiency). Colors representation is the same as for CdTe structures. Tab.5 shows model CIGS solar cells parameters deduced in SCAPS from calculated J-V curve.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Voc [mV]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>no shading</td>
<td>591.50</td>
<td>32.10</td>
<td>79.18</td>
<td>15.04</td>
</tr>
<tr>
<td>5% shading</td>
<td>590.15</td>
<td>30.50</td>
<td>79.16</td>
<td>14.25</td>
</tr>
<tr>
<td>pure ITO</td>
<td>588.28</td>
<td>27.15</td>
<td>66.75</td>
<td>10.66</td>
</tr>
<tr>
<td>ITO on PET</td>
<td>587.27</td>
<td>26.04</td>
<td>66.84</td>
<td>10.22</td>
</tr>
</tbody>
</table>

### Tab.5. Simulated parameters for CIGS PV structure.
Determined characteristics, as in the case of CdTe based PV structures, for CIGS also indicate negative influence of ITO layers on photovoltaic cell performance.

4. Conclusions and further possible solutions

Simulation results, shown in chapter 3, together with a huge resistance instability observed during dynamic bending, presented in chapter 2, lead to search for a different material, characterized with more suitable parameters. There are some proposals studied by Polish and international research teams. One of them is using Al doped ZnO (ZnO:Al) which is more flexible than ITO and its sheet resistance is less bending dependent (Fig.15) [3].

Another investigated solution is application of carbon nanotube (CNT) composites as TCL. It was proved that they are fully flexible and their resistance is almost 100% insensitive for bending (Fig.16) [3].

However, carbon nanotube composites obtain higher optical transmission at lower CNT content, which in turn increases its resistance. Thus, the simultaneous increase of the transmission and resistance reduction is a difficult issue.

Since the discovery of graphene (2010), there is an increasing interest observed in its manifold field of applications. Several experiments are currently conducted with this material including its possible application as transparent conductive layer in flexible photovoltaic structures.

Bibliography


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