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Carbon nanotube transparent conductive layers for solar cells applications

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The paper presents the investigation into a possible new photovoltaic (PV) application of carbon nanotube-based elastic layers, manufactured by a screen-printing technique. The optical and mechanical properties of these layers are investigated and compared with ITO, standard transparent conductive oxide utilized in photovoltaic devices. Simulations of new TCO layer functioning in various solar constructions are performed. Finally, first results of a test silicon cell, contacted by proposed material, are reported.

Keywords: photovoltaics, transparent conductive oxides (TCO), indium tin oxide (ITO), carbon nanotubes, screen printing, flexible layers.

1. TCO layers in photovoltaic applications

Thin-film photovoltaic cells and modules are widely popularized because of their small production costs and relatively high efficiency [1]. Yet some other, significant advantages, like small weight and flexibility of polycrystalline construction, may be offered. Flexible photovoltaic modules were achieved on the basis of different cell structures, *e.g.* poly-Si, CIS (copper indium (di)selenide: $CuInSe_2$), CIGS (copper indium gallium (di)selenide: $Cu(In, Ga)Se_2$), CdS/CdTe or organic materials [2–4]. Many of mentioned devices are contacted by transparent conductive oxides (TCO). For this role various thin-conductive metal oxide layers, such as indium tin oxide (ITO), Zn_2O_4, $CdSnO_4$ or ZnO:Al [5, 6], and also CdO, ZnO and $RuSiO_4$ [7], were implemented.

The most popular solution for TCO application is a mixture of tin (IV) oxide: SnO_2 and indium (III) oxide: In_2O_3, the so-called ITO. This material is characterized by high optical transmission of above 90% in visual range and relatively low electrical resistivity of 10 Ω/square–100 Ω/square for thickness of 150 nm–200 nm.

Unfortunately the immanent shortcoming of ITO is the fragility, which leads to fragmentation while bending. Additionally, ITO layers are produced mostly by expensive techniques like sputtering, which influences the final cost of new cell and module structure. Moreover, the indium resources are strictly limited and expected to be exhausted within next fifteen years of exploitation. Thus, fully elastic transparent conductive layer produced by inexpensive industrial technology is needed for further development of large-area flexible solar modules.

2. New technology of carbon nanotube layer production

New materials such as carbon nanotubes, discovered at the end of last century, have attracted extensive attention in many branches of industry. Composites with carbon nanotubes can revolutionize structural materials design and production in construction elements [8, 9]. Recent achievements of the authors in this field of experiments include elaboration of thick-film printed materials [10, 11] and fabrication of functional printed sensors [12] and transparent electrodes for electroluminescence structures [13].

For preparation of composites, multilayer carbon nanotubes have been used. Materials used for printed electronics, in order to enable manufacturing of disposable systems, should be low cost. Therefore, carbon nanotubes synthesized in catalytic chemical vapor deposition (CCVD) were used, which is currently the only method allowing for fabrication of large quantities of material. Presence of other carbon structures and metal catalyst in significant quantity is a side effect of the process. However, either other CNT (carbon nanotubes) obtaining methods or purification and segregation techniques can increase material cost up to a few orders of magnitude.

Fig. 1. HRSEM image of applied carbon nanotubes.

T a b l e 1. Sheet resistance values for samples with different nanotube amount.

Paste No.	CNT content in the composition [%]	Sheet resistance [kΩ/square]
CNT.0.1	0.1	613
CNT.0.25	0.25	28
CNT.0.5	0.5	3.3
CNT.1.0	1.0	0.87

Characteristic dimensions have been determined by scanning electron microscopy (SEM). The average diameter of the nanotubes in material is 10–40 nm and 0.5–5 µm length, however longer structures have also been observed (Fig. 1).

Electrical properties of printed layers have been measured in order to specify a relationship between the content of CNT and sheet resistance. Measurements have been carried out using a digital Keithley 236 multimeter. All samples showed electrical conductivity and were much above the percolation threshold (Tab. 1).

3. Application in PV cells

Samples of TCL (transparent conductive layer), with different CNT content on borosilicate glass substrates were prepared by described technique. For comparison, identical borosilicate glass samples, of 1.1 mm thick and 25 cm^2 area, covered by sputtered 160 nm ITO layer, were taken. As a first step of carbon nanotubes TCL application in solar cell structure, transmittance of printed layers has been measured (Fig. 2).

A very important observation for printed layers is stability of the resistance while applying multiple mechanical stress. To verify this parameter for manufactured CNT layers, an additional experiment was undertaken. 1.5 µm layer was screen-printed on

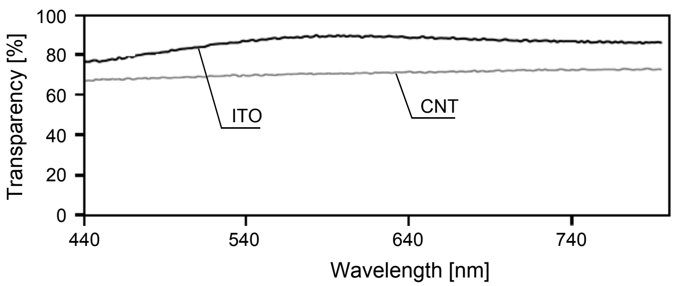

Fig. 2. Transmittance comparison of 0.25%, 1.5 µm CNT layer and 160 nm ITO on borosilicate glass, for standard solar cell absorption spectrum.

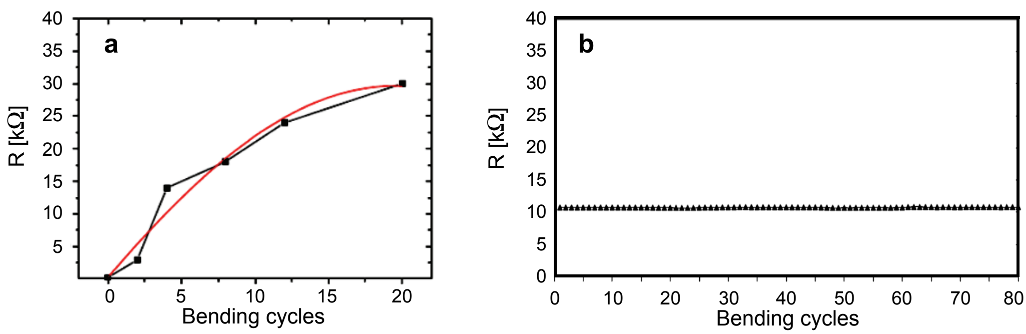

Fig. 3. Resistance changes of ITO [14] (**a**) and manufactured CNT layers (**b**) while bending.

pollimide Kapton® and tested by rapid mechanical bending in 80 cycles. The results of resistivity change (Fig. 3**b**) was compared with literature outcomes, obtained for optical ITO layer (Fig. 3**a**).

After positive evaluation of optical and electrical parameters of manufactured CNT layers, the possibility of implementation as a solar cell transparent conductive coating was verified. For simulations of TCO replacement by screen-printed CNT layer in various solar cell structures, SCAPS (solar cell capacitance simulator) program was used. This simulation package is equipped with advanced tools for *I–V*, QE (quantum efficiency) and carrier transport simulations [15]. Simulation models are generated by digital description of physical parameters of each structure layer, including contacts. Program SCAPS is constantly developed since 1990 and available free of charge for

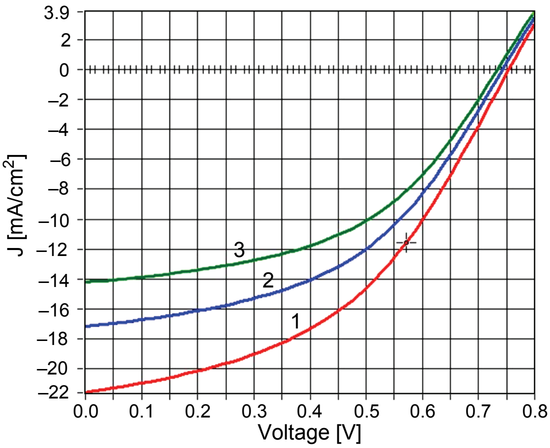

Fig. 4. SCAPS simulations of *I–V* characteristics of CdTe/CdS solar cell with filters: 1 – none, 2 – ITO, 3 – CNT.

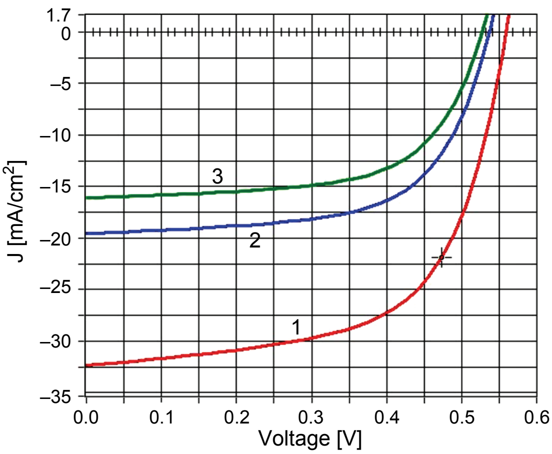

Fig. 5. SCAPS simulations of *I–V* characteristics of Si solar cell with filters: 1 – none, 2 – ITO, 3 – CNT.

T a b l e 2. Electrical parameters of CdTe/CdS solar cell.

Filter	Open circuit voltage V_{OC} [V]	Short circuit current J_{SC} [mA/cm^2]	Fill factor FF [%]	Efficiency η [%]
None	0.754	21.602	44.99	7.33
ITO	0.743	17.194	47.00	6.00
CNT	0.733	14.236	48.50	5.06

T a b l e 3. Electrical parameters of Si solar cell.

Filter	Open circuit voltage V_{OC} [V]	Short circuit current J_{SC} [mA/cm^2]	Fill factor FF [%]	Efficiency η [%]
None	0.621	35.991	83.00	18.53
ITO	0.606	21.010	82.70	10.54
CNT	0.601	17.301	82.70	8.60

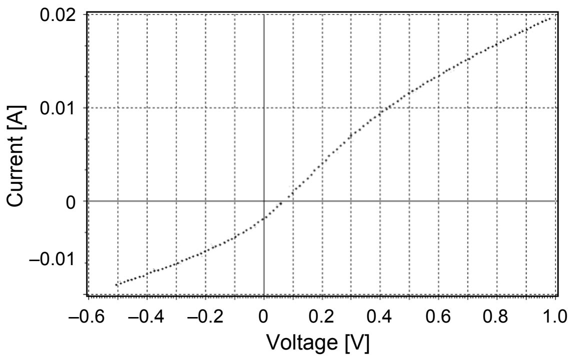

Fig. 6. *I–V* curve measured for Si solar cell under low illumination (100 W/m^2) with CNT front electrode.

scientific research. Figures 4 and 5 present examples of *I–V* curves simulations, respectively for CdTe/CdS and Si solar cell structure with ITO and CNT contact layer. Operating parameters of simulated cells are shown in Tabs. 2 and 3.

Once the possibility of functioning solar cell, equipped with CNT contacts was confirmed by computer simulations, as the last verification stage, practical experiments were carried out. At the preliminary level, standard crystalline silicon solar cell was contacted exclusively by carbon nanotube layer (Fig. 6). The presence of photovoltaic effect was confirmed, however further contact parameter optimization is necessary.

4. Summary and conclusions

Carbon nanotube layer with relatively high optical transmittance was manufactured by an inexpensive screen printing technique on glass and on elastic polymer substrates. The average difference of 10% in transmittance within standard photoconversion range between 160 nm ITO and 1.5 μm 0.25% CNT layer was observed. Sheet resistance of obtained nanotube layers is at relatively high level and should be diminished for efficient photovoltaic application. To achieve this goal, special technology and material compositions (including various CNT content) are tested. The resistance of CNT layers, as opposed to standard ITO, appeared completely independent of bending, which is critical in terms of flexible cells construction. According to computer simulations, the lowest P_m drop, caused by CNT layer implementation, was observed in case of thin-film cells, which is consistent with postulate of new construction flexibility. First, practical experiments confirmed the presence of photovoltaic effect in solar cell equipped exclusively with CNT emitter electrode.

At present, due to weaker optical and electrical parameters, those layers cannot be a competitive alternative to the currently existing transparent conductive coatings such as ITO. Nevertheless, they have much better elastic properties and high prospects for improving the optical and electrical parameters, and therefore they can be potential coatings in solar cells.

Further experiments are planned for development of manufactured structure (including incorporation of main metal contacts) and manufacturing of thin-film cells with carbon nanotube emitter contacts. However, CNT composites obtain higher optical permeability at a lower carbon nanotubes content, which in turn, increases the resistivity of these materials. Thus, the simultaneous increasing of the permeability and reducing the resistivity is a difficult issue.

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