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Comparison of ZnO:Al, ITO and carbon nanotube transparent conductive layers in flexible solar cells applications

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ABSTRACT

In the paper the mechanical, optical and electrical parameters of transparent conductive layers (TCLs) made of carbon nanotubes and metal conductive oxides are explored and compared. All investigated materials are deposited on transparent, flexible polymer foils used for solar cell applications. Obtained results are compared with available parameters of rigid transparent conductive oxides (TCOs) as well as literature reports about Indium–Tin Oxide (ITO) on flexible substrates. Presented paper is a report from the preliminary stage of a new flexible solar cell construction.

1. Introduction

Nowadays flexible photovoltaic modules are available as 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 [1–3].

Most of the above mentioned structures are contacted from emitter side by using thin-layers of transparent and conductive metal oxides, such as ITO, Zn_2SnO_4, Cd_2SnO_4 or AZO (Al doped ZnO) [4,5], as well as CdO, ZnO and $RuSiO_4$ [6]. The choice of material is not obvious – specific requirements of electrical, optical and mechanical properties must be met. The transparent electrode should be characterized by proper values of optical transmission (above 80% for visible spectrum), reflectance (above 60% for infrared range) and electrical conduction [7]. These parameters should be as large as possible, however a necessary compromise is difficult to achieve. The best properties of transparent conductive layers (TCLs) are obtained by modification of the wideband-gap oxide-semiconductors [7]. These materials are usually natural n-type semiconductors due to oxide vacancies in their structure.

One of the most popular materials used as a TCL is ITO, prepared usually by magnetron sputtering deposition. However, availability of indium deposits, the principal material of ITO, is rapidly decreased [8], by growing production of liquid crystal displays (LCDs) and solar cells (the main applications of this material) [9]. It is believed that a shortage of indium will be evident around 2020. In the period of 2004–2007 the price of indium has increased 10 times [10]. Therefore, indium should be substituted by other materials, characterized by similar electrical, optical and mechanical properties.

ZnO was effectively used in optoelectronics due to its simple crystal growth technology, non-toxicity, its abundance and low cost [11]. The material and its variations like ZnO:Al were also successfully adopted as transparent contacts in rigid solar-cell technology, due to relatively good electrical and optical parameters [12,13]. The paper aims at its application as a base for superstrate-configured solar cells, with flexible thin-film structure. In order to verify this possibility, series of experiments related to dynamic mechanical and opto-electrical parameters of flexible ZnO layers was conducted. Alternatively, the utilization of efficient flexible TCL, based

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on carbon nanotube (CNT) films, was proposed and tested in the comparable way.

2. Utilization of carbon nanotube conductive layers

New alternative materials, such as carbon nanotubes, discovered at the end of the last century, have focused attention of technologists from many branches of industry. Recent achievements of the authors in this field include: elaboration of functional printed temperature sensors [14], transparent electrodes for electroluminescence structures [15] and finally thick-film transparent layers on glass [16].

Implementations of carbon nanotube layers as transparent electrodes for display applications indicate the possibility of optical transmittance achievement above 80%, subsequently improved up to 95% [17]. This fact, accompanied by relatively low resistivity, recommends CNT also as a proper material for transparent electrodes for photovoltaic applications. The thesis is also motivated by the reports of high-transmittance CNT layers [18–23].

It is also important (for TCL utilization) that layer's transmittance is negatively influenced by cell high-temperature during long-term exploitation. It is widely known, that within day cycle of operation, temperature of solar module may exceed 70 °C. Combined with seasonal changes, this parameter may strongly limit PV module lifetime by destruction of the encapsulation as well as reduction of transmittance. The CNT layers, manufactured by low-temperature processes, e.g., screen-printing, seem particularly vulnerable to these factors.

3. Description of the experimental conditions

In order to check the influence of temperature on CNT TCL layers, a set of samples, with CNT layers deposited on PET polymer foil and on borosilicate solar-grade glass, was prepared. The investigated layers were obtained by screen-printing and pouring from liquid phase, with 0.25% CNT content in solution of 10% PMMA M_w 350 000 by Sigma–Aldrich. CNT material was obtained by Catalyzed Chemical Vapor Deposition (CCVD), average diameter 8–15 nm, average length 10–50 μm, purity above 95%. The layers of thickness 1–5 μm were tested. An exemplary SEM image of CNT layer is presented in Fig. 1.

Carbon nanotube layers were locally contacted by screen-printed silver paste in order to obtain reliable results of the electrical measurements. It should be noted that the layers were not optimized for lowest resistivity or optical transmittance yet they exhibited sufficient properties to use them as transparent electrodes. The optimization of these parameters is a matter of current work.

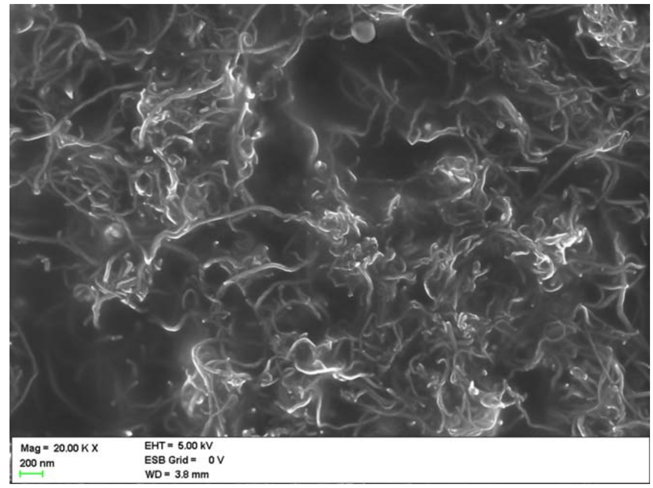

Fig. 1. Exemplary SEM image of obtained CNT layer.

For comparison, standard 160 nm thick ITO (75% In_2O_3 and 25% SnO_2) layers were deposited on the borosilicate solar-grade glass, as it is typical for currently produced thin-film PV modules. In this case ITO layers were obtained using magnetron sputtering method. It was subsequently tested in terms of optical and electrical sensitivity under the influence of temperature changes. Thermal results obtained for ITO are representative for transparent conductive oxides, thus transparent ZnO layers were not tested in this experiment. Samples of ZnO coated polymer foils were utilized in mechanical durability tests.

Climatic tests in Heraeus HT 7012 S2 chamber were conducted according to the engineering standard no. EN 62137, suitable for electronic equipment and solar cells exploitation conditions. Exactly 130 thermal cycles of 1 h each, within −40 to +125 °C temperature range were applied for each sample. After complete climatic tests, optical transmittance within 200–900 nm range as well resistivity of all samples were verified.

In order to investigate bending durability of manufactured TCL layers, series of experiments was conducted for several samples of described above CNT and ZnO:Al coatings. Results were compared

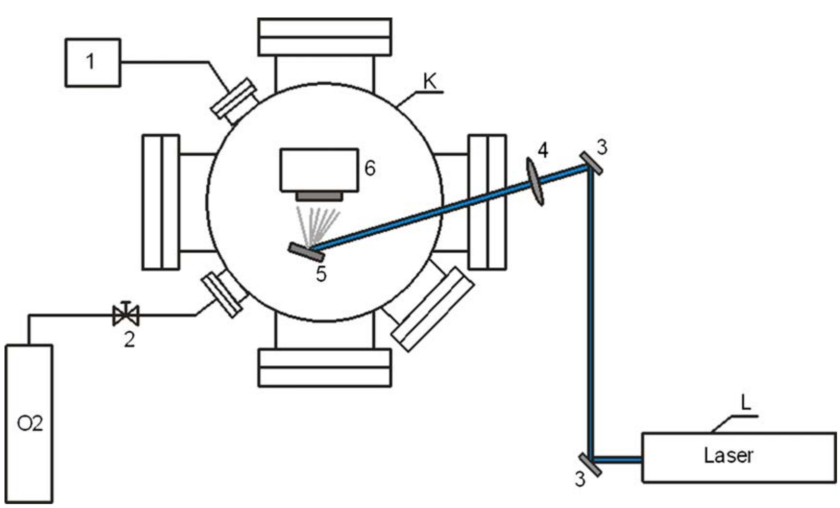

Fig. 2. Experimental setup: (K) vacuum chamber with turbo-molecular pump, (L) laser Nd:YAG, (1) inner pressure control system, (2) O_2 valve, (3) laser beam track, (4) focusing lens, (5) target, (6) substrate on heated basis.