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APPLICATION OF SINGLE-WALL CARBON NANOTUBES AS TRANSPARENT ELECTRODES IN Cu(In,Ga)Se_2-BASED SOLAR CELLS [1]

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ABSTRACT

We present a new thin-film solar cell structure in which the traditional transparent conductive oxide electrode (ZnO) is replaced by a transparent conductive coating consisting of a network of bundled single-wall carbon nanotubes. Optical transmission properties of these coatings are presented in relation to their electrical properties (sheet resistance), along with preliminary solar cell results from devices made using $CuIn_{1-x}Ga_xSe_2$ thin-film absorber materials. Achieving an energy conversion efficiency of >12% and a quantum efficiency of ~80% demonstrate the feasibility of the concept. A discussion of the device structures will be presented considering the physical properties of the new electrodes comparing current-voltage results from the new solar cell structure and those from standard ZnO/CdS/Cu(In,Ga)Se_2/Mo solar cells.

INTRODUCTION

State-of-the-art thin-film photovoltaic (PV) devices incorporate a transparent conductive oxide (TCO) as a "window" layer in their device structure. TCO materials such as ZnO:Al and In_2O_3:Sn (ITO) work relatively well in thin-film PV applications, demonstrated by energy conversion efficiencies of 19.5% attained in $CuIn_{1-x}Ga_xSe_2$-based (CIGS) solar cells [1]. However, TCOs limit the device photo-generated current due to a rather strong free-carrier absorption of infrared (IR) photons. Eliminating this absorption is difficult because it requires reducing the free-carrier concentration [2].

New transparent conductive coatings are needed in thin-film PV technology to provide higher transmittance in the IR portions of the spectrum, while maintaining high electrical conductivity. Other desirable qualities of these new materials are simplicity of deposition, run-to-run reproducibility, and low cost. One type of coating that may be able to achieve this consists of randomly oriented bundles of single-wall carbon nanotubes (SWCNT).

EXPERIMENTAL AND RESULTS

Invisicon® is a transparent conductive coating, produced by EIKOS, consisting of networked bundles of SWCNTs that can be encapsulated in a durable polymer. The coating is made from arc-produced SWCNTs purified by acid reflux, washing, and centrifugation to remove metal catalyst particles and non-tubular carbon. The purified SWCNTs are then dispersed in water and alcohol to form an ink that can be spray coated onto a heated substrate to form an essentially pure SWCNT coating. The morphology of these coatings is characterized by a SWCNT network with random distribution and a high density of voids between bundles of nanotubes. Figure 1 shows a micrograph of a typical Invisicon layer deposited on a CdS/CIGS/Mo/glass substrate.

SWCNT-based coatings have already been used as transparent electrodes in organic PV devices [3]. However, to the best of our knowledge, they have not been employed in inorganic PV devices. The SWCNT-based coatings are highly conductive in thin layers, and optical measurements, such as the transmission data shown in Fig. 2, indicate good transmission (>80%) in the IR (wavelengths >1200 nm) and the absence of free-carrier

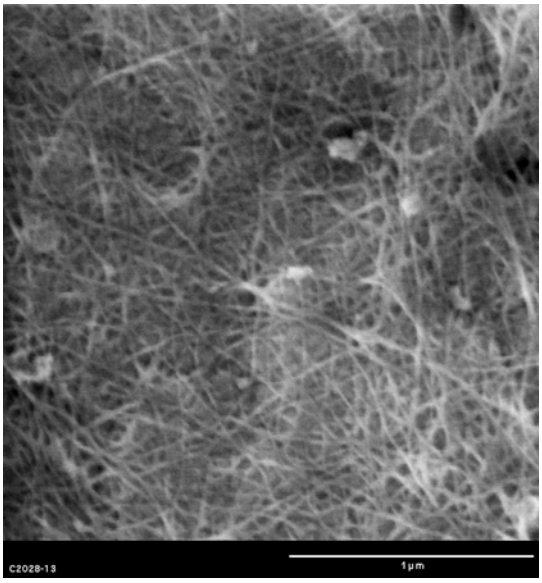

Fig. 1. Morphology of Invisicon (100 ohm/sq sheet resistance) deposited onto a CdS/CIGS/Mo substrate.

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absorption in that region. This characteristic of SWCNT layers is a significant qualitative difference as compared to traditional TCOs such as ZnO and ITO. Figure 2 shows the optical transmission data for comparable sheet resistances of SWCNTs and ZnO. These values of sheet resistances (20–100 ohm/sq) were selected to represent typical values used in solar cells that incorporate a top-contact grid typically made by evaporating Ni (~50 nm) and Al (~3 μm) and deposited over the TCO using a shadow mask.

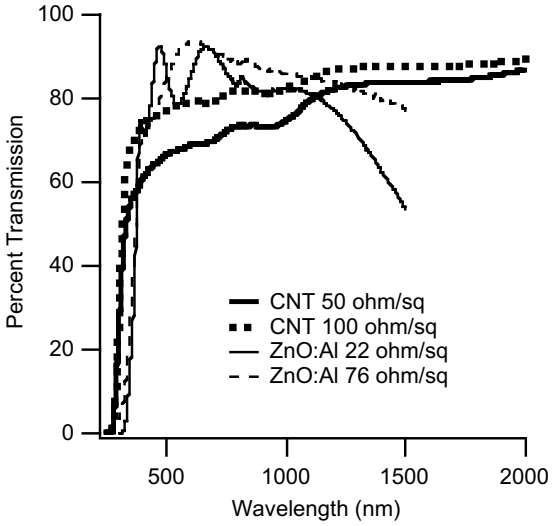

Fig. 2. Optical transmission data in selected SWCNT and n-ZnO layers.

Our standard ZnO/CdS/CIGS/Mo solar cells actually incorporate a bilayer ZnO made of 50–100-nm-thick intrinsic ZnO capped with a 100–130-nm-thick n-type ZnO.

To evaluate Invisicon as a replacement for ZnO, we have fabricated (and tested) device structures composed of varied materials, compositions, and layer thicknesses.

SWCNT/i-ZnO/CdS/CIGS/Mo device structure

We used an Invisicon/*i*-ZnO/CdS/CIGS/Mo device structure (see cross-section view in Fig. 3) to preliminarily evaluate the coatings as a replacement for the n-type ZnO. The CIGS absorber layer was grown by evaporation from elemental sources onto molybdenum coated soda-lime glass. CdS was deposited by chemical-bath deposition. After rf sputtering a thin layer of i-ZnO, the devices were shipped to EIKOS to be coated with 50–100 ohm/sq Invisicon. The coated devices were then returned to NREL, where metal grids were applied and the cells were mechanically scribed and evaluated.

Current density-voltage (J-V) data obtained in initial experiments are summarized in Table 1. We point out that

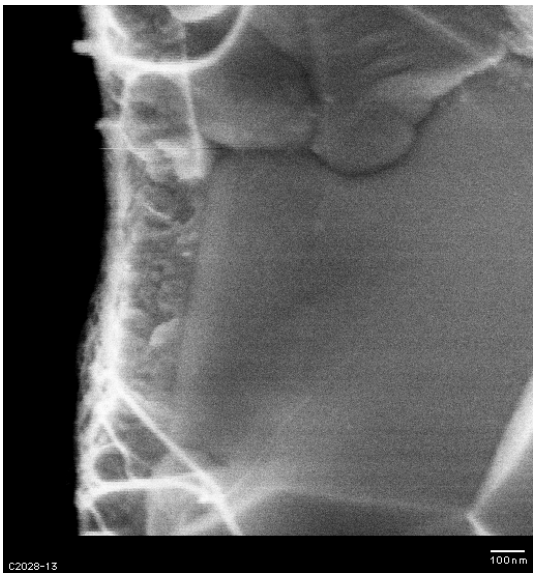

Fig. 3. Cross section SEM micrograph for device structure Invisicon/*i*-ZnO/CdS/CIGS/Mo.

Table 1. Device results for solar cells with structure of Invisicon®/i-ZnO/CdS/CIGS/Mo using varied sheet resistance values for the SWCNT layers. State-of-the-art ZnO/CdS/CIGS values shown in first row for reference

SWCNT (ohm/sq)	Voc (V)	J_{sc} (mA/cm^2)	FF (%)	Eff. (%)	R_s (ohm-cm)	R_{sh} (ohm-cm)
n/a	0.693	35.34	79.4	19.5%	1.449	8798.10
100	0.663	30.43	63.16	12.74	5.072	736.30
100	0.674	31.21	61.66	12.98	5.826	596.70
100	0.680	29.75	63.26	12.79	5.643	1158.84
75	0.650	28.34	61.67	11.3	3.2	165.47
75	0.621	29.71	62.23	11.4	3.25	216.92
75	0.622	29.12	64.93	11.7	3.22	510.78
50	0.598	25.02	62.13	9.30	3.656	265.05
50	0.593	25.03	61.75	9.17	4.08	244.17
50	0.593	25.10	61.65	9.18	4.141	242.90

the device structure, absorber film, and device processing have not yet been optimized, and the data presented herein should be considered preliminary in nature.

The data in Table 1 show two shortcomings in the new device structure: (a) lower short-circuit current density (J_{sc}) values as compared to standard and similar devices incorporating n-ZnO, and (b) low shunt resistance, possibly associated with the thickness of the SWCNT coating (usually <100 nm for those sheet resistance values) and the morphology (voids) that could allow short circuiting between the metal grid and the layers underneath the Invisicon.

The lower J_{sc} values can be directly attributed to the *overall* lower internal quantum efficiency (QE) of the new structures (see Fig. 4). Although the SWCNT coatings are more transparent in the IR than n-ZnO:Al, they are less transparent in the visible and ultraviolet (UV) regions for equivalent sheet resistance (see Fig. 2) . The lower optical transmission across the UV, visible, and up to ~1200 nm contributes strongly to the loss in QE. In other words, some of the photons that could generate photocurrent are absorbed in the SWCNT layer before they reach the electronic junction of the device.

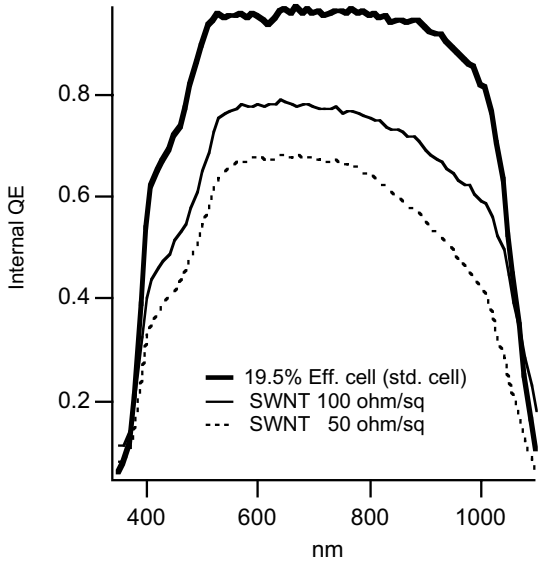

Fig. 4. Internal quantum efficiency of SWCNT/i-ZnO/CdS/CIGS/Mo structures using Invisicon layers with different sheet resistance values. The 19.5%-efficiency cell data are for a standard solar cell (using n-ZnO) and are shown for reference.

Invisicon /CdS/CIGS/Mo device structure

It is of technological interest to simplify the device fabrication process by completely replacing the ZnO bilayer using another robust, low-cost, high-throughput, and scalable approach, such as the one described here. For this purpose, we have fabricated Invison/CdS/CIGS/Mo test structures incorporating varying CdS thickness and obtained the J-V characteristics (a selected set of J-V curves are shown in Fig. 5).

In general, the J-V data obtained indicate a much lower performance (efficiency <4%) and a different behavior as compared to the previous structure incorporating i-ZnO. The lower performance arises from a significant reduction in the open-circuit voltage (V_{oc}) and fill factor (FF) parameters (as seen in Fig. 5). It seems the i-ZnO (absent in these structures) plays a role in mitigating some of the shunting and recombination issues observed. This argument is also supported by the J-V data obtained for devices using thicker (than standard) CdS layers. The thicker CdS also mitigates, to a certain extent, the shunting and loss of V_{oc} and FF, as seen in Fig. 5.

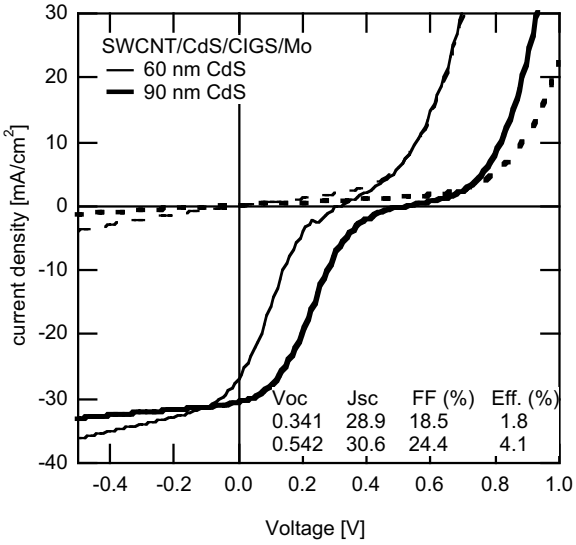

Fig. 5. Effect of CdS thickness on device performance for the 100 ohm/sq SWCNT/CdS/CIGS/Mo structures.

Emulating the electrical characteristics of the ZnO bilayer by using SWCNT layers and Parylene-N

For the reasons mentioned above, we decided to build a device structure that mimics the electrical qualities of the ZnO bilayer; that is, we deposited a high sheet resistance layer on top of the CdS, followed by a highly conducting layer. To achieve this effect, test structures were built using 1000 ohm/sq SWCNT layers on top of the CdS, capped by a thin layer (100–200 nm) of Parylene-N. Parylene-N is a highly insulating polymer used in conjunction with the 1000 ohm/sq SWCNT layer to replace the i-ZnO film. This high sheet resistance composite layer was subsequently capped with highly conductive SWCNT (100 ohm/sq).

The J-V data obtained (e.g., see Fig. 6) indicate a significant improvement in performance when compared to using no Parylene-N (as in the previous case). The best

cells we made using this approach showed energy conversion efficiency >8%. As an example, the J-V parameters for the device data shown in Fig. 6 are: V_{oc}=0.676 V, J_{sc}=23.9 mA/cm^2, FF=45.48%, and efficiency=8.2%.

Evidently, the performance is still lower than structures incorporating i-ZnO; but, as previously mentioned, these structures have not been optimized (neither in thickness nor in sheet resistance values), and they should be considered preliminary. Nevertheless, the approach shows potential for additional improvements and demonstrates that the ZnO bilayer can be completely replaced by SWCNT-based layers.

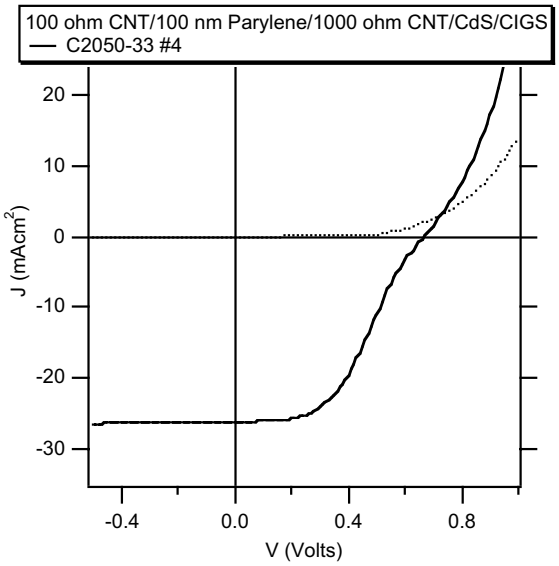

Fig. 6. J-V characteristics of solar cell test structure incorporating Parylene-N.

CONCLUSIONS AND FINAL REMARKS

SWCNT electrodes warrant further study in thin-film PV devices. It may be possible to increase the optical transmission with a correlated reduction of resistivity in the SWCNT coatings by diameter, length, and metallic selection and improvement in the network morphology. Alternatively, the simplicity of the deposition process for SWCNTs and the low cost of the coatings may offset the loss in efficiency. Manufacturing complexity is a significant challenge to the commercialization of CIGS thin-film PV technology. If SWCNT coatings could replace multiple layers of the device (n-ZnO:Al/i-ZnO/CdS), they would greatly enhance the manufacturability and reduce overall module cost.

We have demonstrated that ZnO can indeed be replaced by the approach described in this contribution. Furthermore, due to the unusual optoelectronic properties of the SWCNTs, particularly the high conductivity and superior optical transmission in the IR (>1200 nm) as compared to traditional TCOs, it may be possible to apply them in other PV technologies that utilize more of the IR portion of the solar spectrum. For example, thermo-photovoltaic (TPV) devices and bottom cells in multijunction tandem structures.

Perhaps a more fundamental question is whether SWCNTs can be used as absorber materials as well, that is, as the active material of a solar cell. For this to happen, the tailoring of optical properties (bandgap) and electrical properties (conductivity type) must be addressed.

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