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Citation: *Appl. Phys. Lett.* **94**, 012109 (2009); doi: 10.1063/1.3067819

View online: <http://dx.doi.org/10.1063/1.3067819>

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Specific contact resistance at metal/carbon nanotube interfaces

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(Received 12 November 2008; accepted 13 December 2008; published online 8 January 2009)

In this report, the specific contact resistance between a thin film single wall carbon nanotube electrode and a deposited silver contact was measured. The specific contact resistance was found to be $20 \text{ m}\Omega \text{ cm}^2$, which is an order of magnitude higher than typically observed in standard Si photovoltaic technology. We demonstrate that when utilized as the transparent anode in organic photovoltaics, the specific contact resistance has the potential to induce non-negligible resistive power losses. Thus, specific contact resistance will adversely affect the performance of these systems and should therefore be addressed. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3067819]

Thin transparent films of single wall carbon nanotubes (SWNTs) are an appealing candidate as a surrogate for indium tin oxide (ITO) in organic photovoltaics (OPVs) because of their extraordinary electrical and mechanical properties. Recent reports have demonstrated SWNT thin film electrodes with sheet resistance values as low as $70 \text{ }\Omega \text{ sq}^{-1}$ at 80% transmittance¹ which compare well with commercially available ITO electrodes on polyethylene terephthalate (PET) substrates. Additionally, OPVs with integrated SWNT electrodes have been fabricated with operating device efficiencies comparable to devices made with ITO.²

While SWNT electrodes have shown significant promise as a transparent electrode material, the resistive power losses arising from its sheet resistance remain a considerable barrier to the scaling of OPV devices for large area applications. Both ITO and SWNT electrodes have sheet resistance values comparable to the top emitter used in Si-based photovoltaics (PVs), which can lead to excessive resistive power losses. As a result, the integration of a metallic grid system is required in Si-based PVs to mitigate these losses. Grid systems are comprised of low resistivity metallic fingers and busbars to assist in charge collection from the solar cell and thereby reduce the contribution of the emitter's sheet resistance to system level losses. Due to similar concerns in the use of SWNT electrodes in OPVs, a metallic grid deposited on SWNT electrodes may also effectively reduce the lateral path that photogenerated electrical charges must traverse in the SWNT network before they are collected in low resistance metal fingers [Fig. 1(a)].

In considering carbon nanotube electrodes, an additional resistive loss is formed at the interface between the SWNT electrode and the metal in the form of contact resistance (R_c). Figure 1(b) illustrates the path of device current and the associated resistances within the SWNT electrode and at the metal/SWNT interface. Current crowding occurs at the edge of the metal contact due to the contribution of both R_c and sheet resistance (R_{sh}) resulting in a nonhomogeneous flow of current from the SWNT film to the metal. The length over which $1/e$ of the current has been transferred to the metal contact is described as the characteristic transfer length (L_T). Because R_c is inherently dependent on the area of the contact

interface, the specific contact resistance (ρ_c) is used to evaluate the quality of electrical contacts independent of area. Therefore, in order to achieve minimal resistive power losses, it is essential that a low specific contact resistance exists between the SWNT film and the metallic fingers deposited on the electrode surface. This report will quantify ρ_c at the interface of metallic fingers and a randomly distributed SWNT network, providing the first reported data on this parameter. In addition, this study will also project the impact on power losses due to contact resistance in OPVs.

The transfer length method (TLM) is a common and reliable technique to simultaneously extract the contact resistance, transfer length, and sheet resistance from measured quantities to derive ρ_c . The TLM test structure employed in this study consisted of multiple silver contact pads deposited via electron-beam evaporation onto the SWNT film. A shadow mask was used to define the contact pads at spacings (d_i) of 0.09, 0.29, 0.49, and 0.69 cm. The length (L) and width (W) of the contact pads were 0.1 and 1 cm, respectively, as illustrated in Fig. 2. The total resistance (R_T) was measured between silver pads for each contact spacing and plotted versus d . A sample least-squares fit of R_T is shown in Fig. 2 and can be approximated by³

$$R_T = 2R_c + R_{sh} \frac{d}{W}. \quad (1)$$

For electrically long contacts, such that $L > 2L_T$, R_c can be shown to be equal to⁴

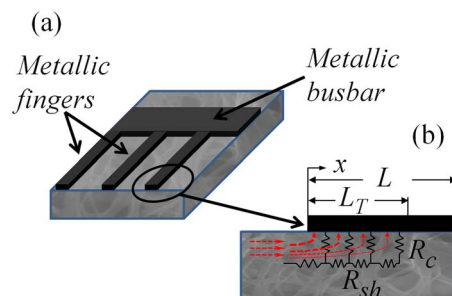


FIG. 1. (Color online) (a) Illustration of metallic grid deposited on SWNT film. (b) Schematic of current and resistance distribution in electrode and electrode/contact interface.

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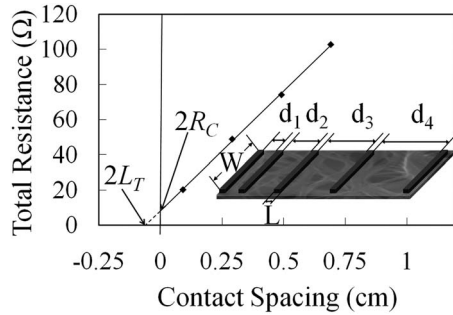


FIG. 2. TLM test structure with a representative plot of R_T vs d illustrating extraction of R_c and L_T .

$$R_c = \frac{R_{sh}L_T}{W}, \quad (2)$$

with L_T defined as

$$L_T = \sqrt{\frac{\rho_c}{R_{sh}}}. \quad (3)$$

The extraction of R_{sh} , R_c , and L_T from Eqs. (1) and (2) permits the determination of ρ_c from Eq. (3). To validate the utility of the TLM in this application, Ohmic contact between the metal pads and the SWNT film was verified with the observation of a linear current/voltage relationship in both forward and negative biases. Silver was selected as the contact metal because of its ability to form Ohmic contact with SWNT networks and its present application in Si-based PV grid systems.⁵

Because p doping of SWNT films via chemical treatment has been demonstrated as an effective method to improve the conductivity of SWNT electrodes,^{6,7} the films in this study were chemically doped to ascertain the influence of this procedure on ρ_c . SWNT films were doped through a multitreatment process consisting of immersion in HNO_3 followed by immersion in SOCl_2 to provide added conductivity enhancement as described by Jackson *et al.*⁶ The average sheet resistance of doped SWNT films with 82% transmittance at 550 nm was $200 \text{ } \Omega \text{ sq}^{-1}$ compared to $350 \text{ } \Omega \text{ sq}^{-1}$ for undoped films.

The resulting average values of L_T and ρ_c of undoped and doped SWNT films with silver contacts are shown in Table I. In both cases, L_T was experimentally found to be less than half of the contact pad length, which justifies the assumption of an electrically long contact in the application of Eqs. (2) and (3). The specific contact resistance for the undoped film was found to be lower than that for the doped film. This result is in contrast to traditional metal/semiconductor contacts that exhibit a decrease in ρ_c with increased charge doping due to the decrease in the effective barrier height at the metal/semiconductor interface.⁸ However, in the case of doped SWNTs, charge transfer at the

TABLE I. Specific contact resistance and transfer lengths of undoped and doped SWNT films with silver contacts.

	L_T (cm)	ρ_c ($\Omega \text{ cm}^2$)
Undoped SWNT film	0.008	0.020
Doped SWNT film	0.021	0.091

metal/SWNT interface is significantly modified when compared to the undoped case. In the undoped SWNT film, a majority of the current is carried by SWNTs that exhibit metallic behavior,⁹ which typically comprise about one-third of the nanotube composition. Therefore, the electrical nature of the undoped SWNT film and metal contact interface is also primarily determined by the interaction of the metal and metallic nanotubes where there is no barrier height to charge transfer. Consequently, the contact resistance at the interface is a factor of the lack of intimate contact over the contact pad area since electron-beam deposition is not sufficient to provide conformal coating of the SWNT network, in addition to any local chemistry between the two surfaces.

After degenerate doping through chemical treatment, the Fermi level of the SWNT film is shifted below the S1 van Hove singularity of the semiconducting SWNTs.⁶ As a result, the semiconducting SWNTs exhibit metallic conduction behavior and thereby carry a larger percentage of the overall current than in the undoped case. Degenerately doped semiconducting SWNTs create additional conduction pathways that function in parallel with existing metallic SWNTs to effectively reduce the overall resistance to lateral current. This phenomenon is evidenced by the decrease in sheet resistance seen in this study and other reported doping treatments to SWNT films.⁷ Therefore, in the doped film, the contact resistance at the metal/SWNT film interface has a significantly larger contribution from metal/semiconductor contact, which is typically a function of the difference of the metal work function and the majority carrier band edge of the semiconductor. The work function of silver is about 4.7 eV,¹⁰ compared to 4.8 eV (Ref. 11) for undoped SWNTs. The majority carrier band edge in semiconducting SWNTs is equivalent to the location of the S1 van Hove singularity. The SWNTs in this study were produced via arc discharge with a mean diameter of 1.4 nm and a typical S1 van Hove singularity position of 0.3 eV from the intrinsic Fermi level position, as derived from tight binding model calculations. Therefore, the difference in the Fermi level of silver and the van Hove singularity for hole conduction is significant, resulting in an increased barrier height to charge transfer to the silver surface for semiconducting nanotubes in comparison to metallic nanotubes. Furthermore, acid treatment can impact the local chemistry between the SWNT film and the silver contact to affect the overall contact resistance. As a result, in the doped SWNT film and silver contact case, the contact resistance is augmented by both the effects of acid treatment and the additional contact resistance of doped semiconducting SWNTs in contact with the silver pad. The higher specific contact resistance observed in this study is consistent with this understanding of the electrical conduction in SWNT films and its corresponding impact on the interfacial resistance.

When considering the impact of ρ_c on PV Ohmic losses, the power loss due to contact resistance (P_{cont}) can be normalized to the maximum output (P_{out}) of the cells. P_{out} is estimated from current state of the art OPVs with device efficiencies of 5.1%.¹² At maximum power, the voltage (V_{mp}) and current density (J_{mp}) were estimated to be 0.425 V and 12 mA/cm², respectively. The fractional losses due to contact resistance (p_{loss}) can be computed from

TABLE II. L_T , p_{loss} , and ρ_c for metal contacts on SWNT electrodes, ITO, and the emitter layer in silicon-based PVs.

	ρ_c ($\Omega \text{ cm}^2$)	L_T (cm)	p_{loss} (%)
SWNT/silver	0.020	0.008	2.82
ITO/silver	0.008	0.011	0.82
Si-PV/silver	0.001	0.005	0.23

$$p_{\text{loss}} = \frac{P_{\text{cont}}}{P_{\text{out}}} = \frac{(JA)^2 R_c}{JAV}, \quad (4)$$

where A is the area between metallic fingers. The finger separation was chosen to be 0.4 cm such that resistive power losses from the electrode sheet resistance can be limited as shown by Rowell *et al.*² The computed results for silver contacts on SWNT electrodes are shown in Table II. For comparison, L_T , ρ_c , and the fractional losses for silver lines deposited onto ITO and for screen printed silver contacts on the top emitter layer in silicon PVs (Ref. 5) are also shown in Table II under similar device operating conditions. The specific contact resistance and transfer length for silver contacts on ITO were derived from the TLM in a similar manner as SWNT/silver contacts described in the previous discussion. The specific contact resistance is higher for an undoped SWNT film in contact with silver than for ITO and more than an order of magnitude higher than silicon-based PVs with a typical specific contact resistance of 1 m $\Omega \text{ cm}^2$ and sheet resistance of 40 $\Omega \text{ sq}^{-1}$.

In summary, the specific contact resistance of a SWNT film in contact with a silver contact pad was found to be significantly higher than typical values obtained in silicon-

based PV applications, resulting in non-negligible power losses. Higher ρ_c can be attributed to the deviation from ideal planar contact of a SWNT mat in contact with silver surface, local Schottky barrier formation at the interface of the silver contact and semiconducting SWNTs, and any local chemistry between the SWNT surface and silver. However, while this work provides the first reported measurement of ρ_c at this interface, no optimization has been performed, thereby providing an opportunity for reduced contact resistance with further research.

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