Optimizing Carbon Nanotube Contacts for Use in Organic Photovoltaics

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OPTIMIZING CARBON NANOTUBE CONTACTS FOR USE IN ORGANIC PHOTOVOLTAICS

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ABSTRACT

Transparent electrical contacts (TCs) play an important role in thin film photovoltaics (PV), including in organic devices (OPV). OPV devices have different TC requirements than traditional thin film devices, due to the need to make them flexible, cost and manufacturing constraints, and the potential benefits that may be realized from using a hole conducting TC. Additionally, the active layer in an OPV device is far thinner than in an inorganic “thin-film” device, causing TC morphology to have a significant effect on device performance. Here, we present data on optimizing carbon nanotube networks for use as TCs in OPV. We look at network deposition techniques and required post-treatment methods along with electrical, optical, and morphological data to devise a fabrication process for a high quality network that is compatible with OPV device production.

INTRODUCTION

Several groups have proposed replacing traditional transparent conducting oxides (TCOs) with thin films made of single-wall carbon-nanotube (SWCNT) networks.[1-4] These SWCNT films can be deposited successfully on flexible substrates using low-cost, low-temperature deposition methods. One major advantage of the SWCNT films over TCOs such as In₂O₃:Sn (ITO), ZnO, and SnO₂ is that their fabrication process readily produces a preferentially hole-conducting contact.[5] This is particularly advantageous in OPV devices, and we have achieved efficient devices in which the SWCNT network replaces both ITO and PEDOT:PSS in a typical bulk heterojunction device.[6] Others have also had success replacing the ITO layer in a bulk heterojunction device on a flexible substrate[7] and augmenting the ITO layer on glass with a SWCNT film.[8] In addition to our work on OPV, we have also successfully replaced the ZnO bi-layer in an efficient CuIn₂Se₃/CdS (CIGS) device and replaced the ITO back contact in a transparent CdTe device.[9, 10] Previous work on p-GaN indicates that SWCNT network electrodes can produce an ohmic contact to a p-type semiconductor. [5] Transparent SWCNT networks have also been incorporated into flexible, transparent transistors,[11] organic light-emitting diodes (OLEDs),[12] and chemical sensors.[13]

Bulk SWCNTs contain a random distribution of differing lengths, diameters, and chiralities. This distribution generally consists of about two-thirds semiconducting tubes and one-third metallic tubes. The tubes can be made by a variety of methods including chemical-vapor deposition, laser ablation of a graphite target, and electric-arc decomposition of a target. As produced, the tubes are intermixed with large amounts of amorphous carbon and metallic impurities (e.g. Ni, Co), both of which must be removed before the tubes are useful for electronic applications. [14] A variety of purification procedures are used, but most rely on an acid reflux that can unintentionally (but often beneficially) dope the semiconducting tubes p-type.[15] This, along with doping from atmospheric impurities, [16] is thought to influence the optoelectronic performance of the films. The carrier concentration in the networks is very difficult to assess, and work is ongoing in this area.[17] It may be possible to determine carrier density from a free carrier absorption edge in the IR, and optical probes of mobility are being investigated. Preliminary data indicate that the mobility is low.

Transport in SWCNT networks is poorly understood, but it seems that some basic concepts from traditional TCOs may prove helpful in improving their performance. SWCNT networks can be doped to improve conductivity, but the actual function of chemical dopants in the networks is not well understood. TCO performance data suggest that improving mobility in the networks should be a major thrust of future research.

It is important to compare the optical and electrical properties of SWCNT networks with the TCOs that they may potentially replace in OPV including ZnO and SnO₂ in addition to ITO. Figure 1 illustrates the differences in optical and electrical properties between a commercial SWCNT network (produced by Eikos, Inc.), SWCNT networks made at NREL by different techniques, and the most commonly used TCOs for PV devices. There are several critical differences between the TCOs and the SWCNT TCs. First, the visible transmittance of the SWCNT TCs is generally lower than that of the TCOs, and many groups are working to improve this. Also, the transmission of the SWCNT TCs in the near infrared is dramatically higher than that of the TCOs because the SWCNT TCs do not exhibit free carrier absorption at these wavelengths. The transmission of the NREL produced electrodes is rapidly approaching that of the commercial material. In addition to comparing Rs and transmission, it is critical to keep in mind any deposition constraints imposed by the device or manufacturing process when comparing different TCs. For example, it is misleading to compare a flexible SWCNT network deposited at room -
temperature to a high-temperature sputtered or CVD grown TCO film on glass if the desired application requires an electrode grown at room temperature on a flexible substrate.

In this report, we study film morphology, conductivity, and optical properties of the networks in order to produce a high-performance transparent contact that is well suited to deployment in high-efficiency OPV devices. We also study the effects of different device processing parameters.

**EXPERIMENTAL METHODS**

We compare two deposition methods for SWCNT network TCs. One fabrication procedure is a straightforward adaptation of a literature method.[1] First, carbon nanotubes are produced at NREL by pulsed laser vaporization (PLV). The as-produced tubes are then purified via acid reflux and sonicated with various surfactants to disperse them into solution. These solutions are then diluted in large quantities of DI water and carefully poured onto a mixed-cellulose ester membrane in a filtration flask. The solution is filtered through the membrane and a glass frit and then rinsed with 100 ml of DI water to remove the surfactant. The membrane can then be acid treated (as will be discussed later) or used directly to produce an electrode. The SWCNT network can be transferred to a substrate or an existing device by wet pressing or an acetone vapor bath. Acetone vapor bath transfer is preferable for transferring directly onto existing polymer layers because it does not rely on water to accomplish the transfer.

The second method for producing the networks uses ultrasonic spray deposition. Ultrasonic spray is readily scalable and amenable to patterning and deposition on flexible substrates, which makes it potentially suitable for large-scale manufacturing. We use the same purified PLV grown SWCNT as for the membrane transfer. The tubes are dispersed into an ink solution using one of several surfactants into an aqueous solution using an ultrasonic bath. We,[18] and others,[19] have seen that the mixing conditions in the ultrasonic bath can affect the electrode properties. The ink is then sprayed onto a gently heated substrate to form the TC and dry the film. To date, we have deposited only on glass substrates.

Network TCs made by both deposition processes generally require some sort of post-treatment process to improve their conductivity. In the membrane process, the surfactant is removed by copious rinsing through the membrane before it is used to transfer the film. The networks made this way can also be doped by soaking in acid, and this can be done before or after the film is transferred to the substrate. Some films/membranes were rinsed before use in OPV devices to study the effects of residual acids on device performance. The spray deposited networks are generally soaked in isopropyl alcohol after deposition, and then rinsed in DI water. The network TCs were characterized using a variety of techniques including spectrophotometry, four-point probe, atomic force microscopy (AFM), and optical microscopy.

These devices were all made in the standard configuration where the SWCNT network was deposited directly on a glass substrate. The network TCs were ultrasonically cleaned in isopropyl alcohol for 5 minutes. The ITO reference device was ultrasonically cleaned in acetone and then isopropyl alcohol for 5 minutes each, followed by a 5 minute oxygen plasma clean. Poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS, Baytron 4083) is often used as a hole transport layer in OPV devices on ITO coated substrates, and we deposited it on several of the SWCNT networks by spin-coating twice at 4000 rpm for 60 seconds each. Some of the coated networks and the ITO reference device were then annealed. The devices were transferred into the glovebox, where the active layers were deposited. The best devices were made using 1:1 mixtures of poly(3-hexylthiophene): phenyl-C61-butyric acid methyl ester (P3HT:PCBM) in dichlorobenzene at a concentration of 25 mg/mL spun on at 200 rpm and slow dried, or “solvent annealed”,[Li, 2007 #924] in a covered glass petri dish for several hours. The devices were then annealed at 110°C for 10 minutes in the glove box and transferred to a thermal evaporator where they were coated with 20 nm of Ca and 100 nm of Al to form the back contact. The devices were then tested on a solar simulator in the glove box.

**RESULTS AND DISCUSSION**

**SWCNT Network Characterization**

SWCNT network TCs produced by the membrane transfer process were used for our initial attempts to produce OPV devices. The networks were highly conductive, especially after treatment with HNO3 or SOCl2. However, the devices always failed when made on the acid treated networks due to wetting problems and adhesion failures of the active layer. Building devices on networks that had not been acid treated was also generally unsuccessful. These networks were more resistive by a factor of about two (140 Ω/sq for an “as-produced” network and about 70 Ω/sq for a SOCl2 treated network), which should have reduced efficiency, but not killed the devices entirely. The
devices all function as resistors, meaning there is likely a direct short between the top and bottom contacts.

Figure 2a shows an AFM image of a typical SWCNT network produced by membrane transfer over a 20 μm² area. Although the networks are generally flat over this area, there are several large-scale features that are over 500 nm in height. The features range in size from small chunks to long thin wrinkles which are likely induced by imperfections in the membrane transfer process. It is difficult to tell whether texturing from the membrane itself plays a role in the film morphology. Remembering that the active layers in these devices are only 200-300 nm thick, an electrode with 500 nm features could clearly induce shorts in the devices.

The AFM image in Figure 2b illustrates the difference in morphology between sprayed and membrane transferred films produced at NREL. The sprayed film shown in a 10 μm scan in Figure 2b is smooth and almost featureless with a maximum feature height on the order of 50 nm. It is wrinkle free with a very uniform morphology that is typical of our spray deposited films. This film was taken from the set used to make the devices described in this work.

The sprayed SWCNT network TCs used in efficient devices were first soaked in HNO₃ overnight, then rinsed three times in DI water to remove residual acid. Acid-soaked films have a sheet resistance of about 60 Ω/sq, and this value increases to about 108 Ω/sq after the water rinsing. Transmission spectra for a doped and subsequently rinsed film are given in Figure 4. The spectrum for the rinsed film shows an average transmission of 77% across the visible range. Absorption peaks due to fundamental excitonic transitions of the SWCNTs around 650 nm and 950 nm are completely bleached in the as-doped films, but the peaks at 650 and 950 nm return upon rinsing. This indicates a high level of doping in the films, which slightly decreases upon rinsing. This decrease is commensurate with the observed change in sheet resistance.[17]

**OPV Device Fabrication**

Several sets of OPV devices were produced on sprayed SWCNT electrodes. Table 1 contains efficiency (η), opencircuit voltage (Voc), current density (Jsc), and fill factor data for the devices described here. This data is not NREL certified and there are certain caveats associated with measuring small OPV devices like the 0.1cm² devices discussed here. They are not masked, and they are highly susceptible to collection outside the active area of the device, which may artificially inflate Jsc and η. However, the data for the FF and Voc are fairly reliable. We are working on building larger devices that can be effectively masked off for more reliable efficiency measurements.

The first devices made on the sprayed electrodes used drop-cast active layers, yielding devices with good efficiency and very poor reproducibility due to a highly non-uniform active layer thickness. The data for the best drop cast device, with an efficiency of approximately 2.9%, is included in Table 1. This device contained a thin layer of PEDOT:PSS as well.

The best OPV devices in this study were made using the sprayed electrode and very slow spin coating for the active layers (200 rpm). This yields a thicker layer, and the films are very wet after spin coating. Data for these devices is presented in Table 1, including data for an ITO reference and a SWCNT network device without PEDOT:PSS. Current density vs. Voltage curves for these devices are presented in Figure 5. Note that although the Jsc values

<table>
<thead>
<tr>
<th>Device</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drop cast</td>
<td>0.561</td>
<td>9.803</td>
<td>52.95</td>
<td>2.91</td>
</tr>
<tr>
<td>spray</td>
<td>0.572</td>
<td>10.65</td>
<td>57.6</td>
<td>3.5</td>
</tr>
<tr>
<td>ITO</td>
<td>0.571</td>
<td>11.09</td>
<td>55.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Spray w/o PEDOT</td>
<td>0.491</td>
<td>5.4</td>
<td>39.2</td>
<td>1.05</td>
</tr>
</tbody>
</table>
are likely inflated by collection outside the active area, that the FF and Voc values are quite high. All of the values for the SWCNT device (with PEDOT:PSS) and the ITO reference are very similar, and the data are highly reproducible.

The device without PEDOT:PSS shows poor performance compared with the others, but it is a rectifying device with measureable efficiency. The device made without PEDOT:PSS exhibits a much lower Voc and FF than the devices made with it. This may be due a combination of the lower workfunction of the SWCNT bare electrode compared to PEDOT:PSS and a reduced shunt resistance caused by shorting between the electrode and the active layer.

CONCLUSIONS

SWCNT network electrodes can work well in OPV devices using relatively thick active layers. The SWCNT network must be very smooth, and we find that this is best achieved using ultrasonic spray deposition. The electrode sheet resistance can be relatively high (∼100 Ω/sq vs. ∼10 Ω/sq for ITO) without a significant drop in device performance provided that the network is smooth enough to prevent shorting through the active layer. It is also necessary to thoroughly rinse out any residual acid from the network to prevent damage to the active layer. Currently, PEDOT:PSS is required to yield an efficient device, but it may be eliminated in future devices once alternative means of altering the SWCNT network work function are achieved.

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REFERENCES


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**Subject Terms:** PV; transparent electrical contacts; thin film; organic devices; optimizing; carbon nanotube;