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Improved conductivity of transparent single-wall carbon nanotube thin films via stable postdeposition functionalization

Bhavin B. Parekh, Giovanni Fanchini,[a] Goki Eda, and Manish Chhowalla
Materials Science and Engineering, Rutgers University, Piscataway, New Jersey 08854

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A simple postdeposition method for improving the conductivity of transparent and conducting single-wall carbon nanotube (SWNT) thin films via exposure to nitric acid and thionyl chloride is reported. A systematic study on a range of films of variable density and from different commercial sources of SWNTs is performed. The functionalized films possess sheet resistances as low as that of indium tin oxide (ITO) (~30 Ω/□) albeit at lower transmittance (~50%). At 80±5% transmittance, the functionalized films have resistance values ranging from 150 to 300 Ω/□. The SWNT films, however, are more flexible than ITO. The stability of the functionalized films upon annealing and processing in solvents (water, methanol, and chloroform) is also reported. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2715027]

Transparent and conducting single-wall carbon nanotube (SWNT) thin films are an interesting class of materials.[1] They can be prepared by purifying the nanotubes then transferring them, at room or moderate temperature, onto a substrate using a variety of techniques.[2–4] Their transport properties can be understood in the framework of the percolation theory[1,5] and, therefore, can be tuned over several orders of magnitude by adjusting the density of SWNTs in the network.

Typically, transparency of about 80% can be obtained at sheet resistances of ~0.5 kΩ/□,[1,5] suggesting that they could be promising candidates for replacing indium tin oxide (ITO) in organic electronics.[6,7] Although the sheet resistance of SWNT thin films is still higher than that of a 100-nm-thick ITO layer, the unique morphological features make them efficient hole collectors in organic photovoltaics, allowing conversion efficiencies of up to 2.5%.[7] A decrease in the resistivity of SWNT films would be beneficial for such an application, allowing the possibility of achieving the state-of-the-art efficiencies of up to 5%.[8]

We have recently reported that SWNTs covalently functionalized in phosphorus tribromide (PBr_3) can be used to prepare thin films with improved transport properties.[9] However, the PBr_3 treatment must be performed in a controlled atmosphere and, being incompatible with many types of substrates, it cannot be used for postdeposition treatment of the films. Covalent functionalization of carbon nanotubes in chlorides has also been reported to significantly decrease their sheet resistance.[10] However, in order to use functionalized SWNT thin films in organic solar cells, it is important to study their stability upon thermal annealing and compatibility with the most commonly used solvents in solution processed organic photovoltaics.

In this letter, we report decrease in sheet resistance of SWNT thin films by a factor of 5 via exposure to thionyl chloride ($SOCl_2$). SWNTs from different commercial sources have been used and the results of the treatment were found to be independent of the type of SWNTs. It is worth noting that $SOCl_2$ treatment is compatible with glass and flexible substrates such as polyethilene terephtalate (PET) used in transparent and flexible electronics. The SWNT thin films were prepared using the vacuum filtration method of Wu *et al.*[4] from HiPCO SWNTs purified in our laboratory,[5,11,12] arc-discharge synthesized SWNTs purified by the supplier (P2 type, Carbon Solutions Inc.[13]), and laser-grown SWNTs (CNI, purified using the method of Landi *et al.*[14]). Aqueous solutions at 1 wt % of sodium dodecyl sulfate were used to disperse the SWNTs at a concentration of 2 mg/l. Filtration (through 200 nm Millipore ester membranes) volumes ranging from 10 to 80 ml allowed the depositon SWNT films of different thicknesses and densities.[11] The ester filter membranes were then transferred onto glass or PET substrates, dried in vacuum for 6 h under 250 g/cm^2 load, and etched in consecutive acetone and methanol baths, leaving behind SWNT thin films on the substrates.

The functionalization treatment was carried out by dipping the films for 3 h in an azeotropic nitric acid bath (69.7% in HNO_3) and dried with gentle nitrogen flow. Subsequently, the nitric acid treated films were dipped for an additional 3 h in a $SOCl_2$ bath (97% reagent grade, Aldrich Inc.) and again carefully dried. All the treatments were performed in air at room temperature. The transmittance of the films was recorded at normal incidence using a Perkin Elmer Lambda 20 spectrophotometer. The electrical data were obtained from two-point measurements using ±1 V *I-V* scans at 100 mV/s. The same films were investigated both before and after functionalization using the same contact distance. Thus, the observed decreases in resistance imply a decrease in sheet resistance and an improvement in conductivity of the same magnitude.

The typical decrease in resistance by $SOCl_2$ functionalization at a constant transmittance in one of our films is shown in Fig. 1(a). It can be seen that the sheet resistance decreases after the initial exposure to the 3 h HNO_3 bath and further decreases after contact with $SOCl_2$. Immersion of the film and complete drying leads to instant improvement in the conductivity by a factor of 5. Longer immersion times did not provide any further change in conductivity. In contrast, the transmittance of the thin films was not affected by the $SOCl_2$ functionalization process, as indicated in Fig. 1(b).

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[a] Author to whom correspondence should be addressed; electronic mail: fanchini@rci.rutgers.edu

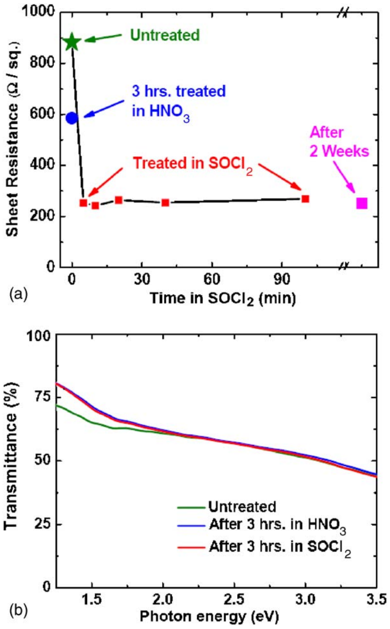

FIG. 1. (Color online) (a) Decrease in resistivity as a function of time for a 40 ml SWNT thin film after HNO_3 and $SOCl_2$ treatments. (b) Transmittance vs photon energy for untreated and HNO_3 and $SOCl_2$ treated SWNT thin films.

The transmittance at 550 nm of $SOCl_2$ treated and the same untreated SWNT thin films as a function of their resistance is plotted in Fig. 2(a). It can be observed that while our untreated SWNT films exhibit properties comparable to those reported in the literature,[1] the $SOCl_2$ functionalized films always exhibit lower sheet resistance at all transparency values. In the densest films, sheet resistance as low as 30–40 $\Omega/\square$ can be achieved, comparing favorably with ITO, albeit at lower transparency. The SWNT thin films are, however, more flexible than ITO, as demonstrated in Fig. 2(b), which shows the *I-V* curves of an ITO and a $SOCl_2$ treated SWNT thin film (50 ml) on PET before and after bending ten times at 45°. During such a test, the resistance of ITO thin film increased by four orders of magnitude while the resistance of the SWNT thin film remained almost unchanged.

We further investigated the role of the preliminary treatment in HNO_3 and the $SOCl_2$ treatment time. Although not essential in influencing the final sheet resistance or transparency of the SWNT thin films, we found that both of these steps are helpful in improving the stability of the functionalized SWNT thin films [see Fig. 1(a)]. In contrast, the absence of the HNO_3 treatment and shorter $SOCl_2$ dipping times led to rapid degradation of the properties under thermal annealing and exposure to air or various solvents relevant for organic electronics. The effects of thermal annealing of the untreated and $SOCl_2$ treated thin films in nitrogen atmosphere are plotted in Fig. 3(a). A similar, relatively low, increase of the sheet resistance with annealing temperature can be observed in both the treated and untreated films. Therefore, the observed reduction cannot be assigned to the massive release of the $SOCl_2$ related functionals, which are probably still strongly attached even above ~250 °C.

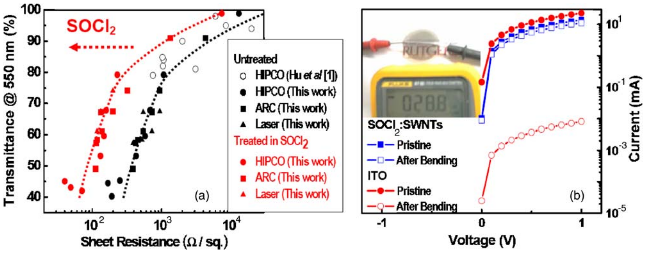

FIG. 2. (Color online) (a) Film transmittance vs sheet resistance for the various films found in the literature (Ref. 1) and investigated in this study (laser, arc discharge, and HiPCO synthesized) and measured after and before the HNO_3-SOCl_2 treatment, and (b) current vs voltage characteristics of ITO and SWNT thin films after bending at 45° ten times. The ITO resistance increase by four orders of magnitude while the SWNT thin film conductivity remains almost unchanged.

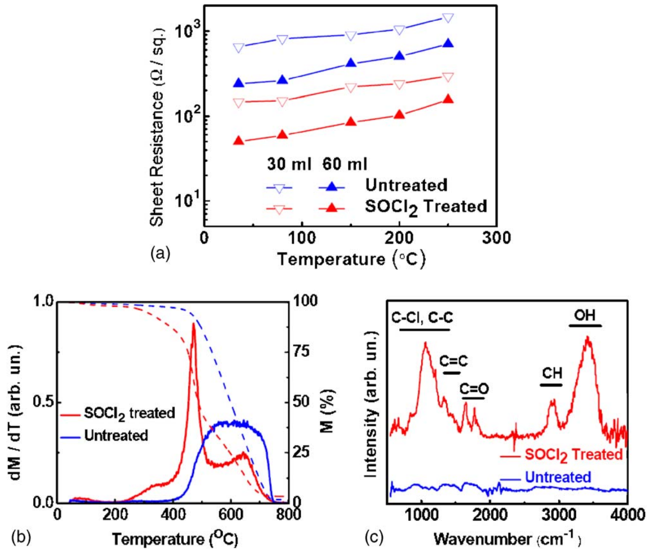

FIG. 3. (Color online) (a) Resistivity as a function of the annealing temperature for untreated and $SOCl_2$ treated films (30 and 60 ml filtration volumes) and (b) TGA in air of untreated and $SOCl_2$ treated films from HiPCO SWNTs (Perkin Elmer Pyris analyzer) reporting mass loss (M, dotted lines) and differential mass loss (dM/dT, solid lines) as a function of temperature. The sharp peak at 450 °C may indicate the release of $SOCl_2$ related functionals. Such a relatively high desorption temperature is a strong indication that the functionals are chemically bonded to the SWNTs. (c) IR spectra of the SWNTs prior to TGA analysis (Nicolet FTIR 6700 spectrometer). The functionalized SWNTs show relatively more prominent peaks, possibly from COOH and COCl attachment.

In order to investigate the effect of temperature on the evolution of $SOCl_2$ functionals in more detail, additional investigation using thermogravimetric analysis (TGA) was performed. Figure 3(b) compares the TGA profiles of untreated and HNO_3-SOCl_2 treated HiPCO SWNTs. The differential TGA curve of the untreated specimen shows one single broad peak at 600 °C, corresponding to the final loss of mass due to the oxidization and sublimation of the SWNTs.[12] In contrast, the TGA curve of the functionalized SWNTs exhibits one additional peak at 450 °C which we assign to the release of functionals related to $SOCl_2$. This compares well with the temperature required for the release of acyl chloride (COCl) radicals in acetyl chloride and other compounds.[15] Since the functionalized SWNT films are stable well above the annealing temperature of organic devices, $SOCl_2$ is likely to be useful for improving the conductivity of transparent SWNT films for such applications.

Further insights into the effect of $SOCl_2$ treatment on the structure of SWNTs was obtained through Fourier-transform infrared spectroscopy recorded prior to the TGA measurements. These spectra are shown in Fig. 3(c). It can be observed that the SWNTs exhibited very weak peaks before

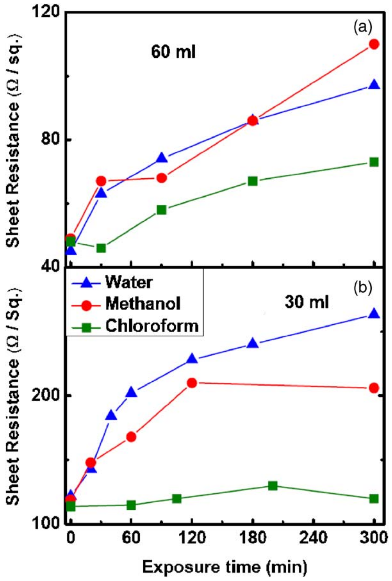

FIG. 4. (Color online) Resistivity as a function of exposure time in solvents for (a) 60 ml and (b) 30 ml $SOCl_2$ treated SWNT thin films from HiPCO SWNTs. The lower sensitivity to chloroform can be observed. Even after 5 h of solvent exposure, the sheet resistivity of the $SOCl_2$ treated SWNT thin films is lower than the corresponding value prior to treatment (i.e., $\sim 250\ \Omega/\square$ at 60 ml and $\sim 950\ \Omega/\square$ at 30 ml).

functionalization but, after the $SOCl_2$ treatment, strongly active C–Cl (950 cm^{-1}), C–C (1050 cm^{-1}), and $C{=}O$ (1700 cm^{-1}) bond stretching modes[16] and activated $C{=}C$ modes [1600 cm^{-1} Ref. 17] can be readily seen. Such vibrations are the result of chemical attachment of functionals to the SWNTs, possibly in the form of acyl chloride groups.

It is interesting to note that, although the treatment in HNO_3 likely introduced some defects at the SWNT ends[18] (and possibly also on the tube sidewalls[19]), it does not appear to have any detrimental effect on the electrical properties of the SWNT thin films. Such a phenomenon could be explained by assuming that the dangling bonds or defects formed by the HNO_3 treatment are immediately passivated by hydroxyl (OH) or carboxyl (COOH) groups.

Furthermore, once OH or COOH groups are put in contact with $SOCl_2$, a nucleophilic substitution by chlorine takes place so that SWNTs bonded with Cl or COCl are produced. As demonstrated by our experiments, such functional groups have beneficial effects on the conductivity of SWNTs. We have shown[9] that acyl bromide functionals, due to their strong electronegativity, act as electron acceptors, tending to move the Fermi level toward the valence band and to increase the hole density in SWNTs. The movement of the Fermi level is expectably much weaker with acyl chlorides than with acyl bromides and this may result in lower hole density and in higher electron density in chlorinated SWNTs compared to brominated SWNTs. However, even under such conditions, chlorinated functionals are able to improve the transport properties of SWNTs. This can also explain the beneficial effects of the preliminary HNO_3 treatment on the thermal stability of $SOCl_2$ treated SWNT thin films. Indeed, in the absence of such treatment, SWNTs are much less defective and most of the $SOCl_2$ is simply physisorbed in the form of Cl^- ions rather than being covalently bonded to the nanotubes. Such physisorbed ions can still dope the SWNTs to increase the conductivity but are relatively unstable when exposed to temperature or air.

We have exposed the SWNT thin films to various solvents used in organic electronics. The stability, in terms of the change in electrical properties, of the $SOCl_2$ treated SWNT thin films dipped in water, methanol, and chloroform was investigated and the results are shown in Fig. 4. It is important to note that our films are relatively stable in chloroform even after prolonged exposure. This is significant because chloroform is widely used for spin-coating the polythiophene-fullerene blends used in organic photovoltaics.[8] In contrast, the conductivity of the $SOCl_2$ treated SWNT thin films decreases faster in water and alcohols, which are known to decompose acyl chlorides. However, as can be observed from Fig. 4, such decomposition is rather slow, occurring during temporal scales which are at least one order of magnitude longer than the time required to assemble an organic solar cell by spin coating.

In summary, we have developed a simple room-temperature postdeposition procedure able to reduce the sheet resistivity of transparent and conducting SWNT thin films to values of $40-50\ \Omega/\square$, which compares reasonably well with ITO, albeit at lower transparency (i.e., $\sim 50\%$ vs 80%). Our films, however, are more flexible than ITO. We suspect that the enhancement in transport properties upon $SOCl_2$ treatment is related to the formation of acyl chloride functionals. We found that the $SOCl_2$ related functionals only slowly decompose in water and methanol, and they are reasonably stable in chloroform and at annealing temperatures of at least 250 °C in nitrogen atmosphere.

[1] L. Hu, D. S. Hecht, and G. Gruner, Nano Lett. **4**, 2513 (2004).
[2] N. Saran, K. Parikh, D. S. Suh, E. Munoz, H. Kolla, and S. K. Manohar, J. Am. Chem. Soc. **126**, 4462 (2004).
[3] Q. Cao, S. H. Hur, Z. T. Zhou, Y. Sun, C. Wang, M. Shim, and J. A. Rogers, Adv. Mater. (Weinheim, Ger.) **18**, 304 (2006).
[4] Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, Science **305**, 1273 (2004).
[5] H. E. Unalan, G. Fanchini, A. Kanwal, A. Du Pasquier, and M. Chhowalla, Nano Lett. **6**, 677 (2006).
[6] A. Du Pasquier, H. E. Unalan, A. Kanwal, S. Miller, and M. Chhowalla, Appl. Phys. Lett. **87**, 203511 (2005).
[7] M. W. Rowell, M. A. Topinka, M. D. McGehee, H.-J. Prall, G. Dennler, N. S. Sariciftci, L. Hu, and G. Gruner, Appl. Phys. Lett. **88**, 233506 (2006).
[8] *Organic Photovoltaics*, edited by S.-S. Sun, N. S. Sariciftci (Taylor & Francis, London, 2005).
[9] G. Fanchini, H. E. Unalan, and M. Chhowalla, Appl. Phys. Lett. **90**, 092115 (2007).
[10] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson, and C. Zhou, Nano Lett. **6**, 1880 (2006); U. Dettlaff-Weglikowska, M. Kaempgen, B. Hornbostel, V. Skakalova, J. Wang, J. Liang, and S. Roth, Phys. Status Solidi B **243**, 3340 (2006).
[11] G. Fanchini, H. E. Unalan, and M. Chhowalla, Appl. Phys. Lett. **88**, 191919 (2006).
[12] H. E. Unalan, Ph.D. thesis, Rutgers University, 2006.
[13] See website: www.carbonsolution.com
[14] B. Landi, C. D. Cress, C. M. Evans, and R. P. Raffaelle, Chem. Mater. **17**, 6819 (2005).
[15] E. H. Huntress, *Organic Chlorine Compounds* (Wiley, New York, 1948), p. 960.
[16] N. B. Colthup, L. H. Daly, and S. E. Wiberly, *Introduction to Infrared and Raman Spectroscopy* (Academic, Boston, 1990), p. 210.
[17] U. J. Kim, X. M. Liu, C. A. Furtado, G. Chen, R. Saito, J. Jiang, M. S. Dresselhaus, and P. C. Eklund, Phys. Rev. Lett. **95**, 157402 (2005).
[18] S. C. Tsang, Y. K. Chen, P. J. F. Harris, and M. L. H. Green, Nature (London) **372**, 159 (1994).
[19] H. Hu, M. E. Itkis, and R. C. Haddon, J. Phys. Chem. B **107**, 13838 (2003).