Chapter 3
Transparent Conducting Films by Using Carbon Nanotubes

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3.1 Introduction

The interests on the flexible transparent conducting films (TCFs) have been growing recently mainly because of strong needs for electrodes of flexible or wearable displays in the future (Cairns and Crawford, 2005). The current technology adopts indium-tin oxide (ITO) for TCFs that meets the requirement of low resistance and high transmittance. Yet, bending of the ITO film generates cracks in the film, resulting in poor flexibility reported by Saran et al. (2004). This is a serious drawback in flexible display applications. Carbon nanotube (CNT), which was discovered by Iijima (1991), is a new functional material that can be treated as graphitic sheets with a hexagonal lattice being wrapped up into a cylinder (Baughman et al., 2002). It has a high aspect ratio of typically 1,000 or greater with a diameter of a few nanometers. It is generally known that CNTs have high elastic modulus of 1–2 TPa as well as high electrical conductivity which is 1,000 times larger than Cu-wire (Bernholc et al., 1998; Salvetat et al., 1999; Mamalis et al., 2004). Wu et al. (2004) found that the CNTs were capable of forming naturally robust random network in the film and provide low sheet resistance and high transmittance with a minimal amount of CNTs. CNT films have been known to exhibit an excellent bending characteristics over the conventional ITO film. These structural and physical properties of CNTs are superb features for flexible TCFs, providing high performance of transparence and conductivity. Although CNTs have been suggested for flexible TCFs with outstanding film performance, the performance strongly relies on the film preparation conditions (Kaempgen et al., 2003; Sreekumar et al., 2003; Kim et al., 2003; Saran et al., 2004; Wu et al., 2004; Ferrer-Anglada et al., 2004; Hu et al., 2004; Zhang et al., 2005; Kaempgen et al., 2005; Moon et al., 2005; Unalan et al., 2006). The understanding for the film fabrication methods, material dependence, and criteria to determine the sheet resistance and transmittance is still in its infant stage.

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The fabrication of TCFs includes three steps: (i) the CNT treatment, (ii) the CNT-solution preparation, and (iii) the film preparation. The choice of CNTs, the degree of purity and defects of CNTs, and further post-treatment of CNTs are presumably important factors in determining the film performance. The CNTs are easily bundled with a diameter of typically a few tens nanometers due to their strong van der Waals interactions (∼1000 eV) originating from the micrometer long CNTs (Thess et al., 1996; Pan et al., 1998; Sun et al., 2005). Thus, the macrodispersion (small-size bundles) or the nanodispersion (dispersion into individual nanotubes) is strongly desired in order to minimize the absorbance (O’Connell et al., 2001; Richard et al., 2003; Lee et al., 2005; Kim et al., 2005). The choice of solvents and the related dispersants are crucial factors in achieving the best dispersion conditions (O’Connell et al., 2002; Vaisman et al., 2006). Once the CNT solution is ready, the film preparation is another important step to consider, since this determines the networking of CNTs.

The purpose of this work is to determine which type of nanotubes is the best for flexible TCFs. Several single-walled CNTs (SWCNTs) prepared by different methods such as arc discharge (Arc), catalytic chemical vapor deposition (CVD), high pressure carbon monoxide (HiPCO), and laser ablation (Laser) were introduced to search for the material parameters. These CNTs were dispersed in water with sodium dodecyl sulfate (SDS) with sonication. This CNT solution was then sprayed onto the Poly(ethylene terephthalate) (PET) substrate by a spray coater to form the CNT film. The quality of CNTs, the degree of dispersion, film morphology and the performance of TCFs were characterized by scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, Raman spectroscopy, optical spectra, and four-point probe measurements. We found that the material parameters such as the diameter and crystallinity of CNTs, bundle size, networking of CNTs of the film, the degree of dispersion of CNTs in solvent are crucial parameters to improve the film performance. We proposed a material quality factor to evaluate the quality of SWCNTs and further discussed the film performance that relied on the absorbance and on the degree of entanglement in the CNT network. Our analysis demonstrates that the Arc SWCNTs are the best candidate to give rise to the lowest sheet resistance and highest transmittance among other species. The CNT film performance shows a good candidate for replacing the conventional ITO transparent conducting film in various application fields.

### 3.2 Experimental

Different kinds of SWCNT materials were used in this study. The CVD SWCNTs were purchased from SouthWest NanoTechnologies, Inc., HiPCO SWCNTs and Laser SWCNTs were from Carbon Nanotechnology, Inc. Arc SWCNTs were from Iljin Nanotech Co. Ltd. The CNTs were characterized by the field-emission scanning electron microscopy (FE-SEM-JSM7000F), transmission electron microscopy (TEM-JEM2100F), Raman spectroscopy (Renishaw RM1000-Invia), and thermogravimetric analysis (TGA-Seiko Exstar 6000 (TMA6100), SEICO INST. JAPAN).
Deionized water was used to disperse SWCNTs with sonication and centrifuge process. SWCNTs with a concentration of 0.3 mg/ml and SDS (Sigma–Aldrich) of 3 mg/ml were dissolved in water and sonicated in a bath type sonicator (Power sonic 505) at 400 W for 10 hours. The SWCNT solution was centrifuged at 10,000 g for 10 minutes by centrifuge (Hanil Science Industrial, MEGA 17R). The upper 50% of the supernatant solution was carefully decanted for characterization. Absorbance of the SWCNT supernatant was recorded by UV-VIS-NIR spectrophotometer (Cary-5000). The SWCNT supernatant was directly sprayed with air brush pistol (GUNPIECE GP-1, FUSO SEIKI Co. LTD) onto the PET substrate. A special care for the choice of CNT concentration was taken in order to keep the nozzle from being clogged.

During the spray process, the PET substrate was kept on the sample holder at 100 °C to accelerate evaporation of the fine droplets on the surface. When the spray process was terminated, the TCF film was immersed into deionized water for 10 minutes to remove the surfactant and dried in a dry oven at 80 °C for 30 minutes. This process was repeated twice to further remove surfactants and enhance adhesion between CNTs and PET film. The transmittance was recorded by UV-VIS-NIR spectrophotometer in the visible range (400–800 nm). Measurements of the sheet resistance were carried out by four-point probe method (Keithley 2000 multimeter) at room temperature.

3.3 Results and Discussion

3.3.1 Analysis on SWCNT Materials

The general properties of SWCNT powders were characterized by different methods. Figure 3.1 presents the FE-SEM and TEM morphologies of different SWCNT powders used in our study. The average diameters of individual CVD, HiPCO, Laser, and Arc SWCNTs were 0.8, 1.0, 1.2, and 1.4 nm, respectively, as determined from the TEM images. The CVD SWCNTs had the smallest average bundle size, as estimated from the SEM images, whereas the Laser sample had the largest average bundle size among all the samples. Some carbonaceous particles on the CNT bundles were present in the CVD SWCNTs. The Arc SWCNTs had relatively well-defined crystallinity without amorphous carbons on the tube walls, although the bundle size of the Laser sample was larger than that of the Arc sample from the FE-SEM images. The presence of carbonaceous particles on the nanotube walls is an important factor for the application of TCFs, since they determine the contact resistance among the CNT network (Dai et al., 1996; Jost et al., 1999; Hu et al., 2006).

The purity of each sample can be obtained from the TGA. Figure 3.2 presents the TGA and differential TGA of the SWCNTs that were used in this work. The SWCNTs started to burn off in air with increasing temperature. The remaining material at 900 °C was metal oxides. All the samples contained some amounts of catalysts. The burning temperature obtained from the peak of differential TGA varied with several
Fig. 3.1 FE-SEM (scale bar: 200 nm) and TEM (inset, scale bar: 20 nm) images of CNTs: (a) CVD SWCNTs, (b) HiPCO SWCNTs, (c) Laser SWCNTs, and (d) Arc SWCNTs

Fig. 3.2 TGA and differential TGA of the CNTs: (a) CVD SWCNTs, (b) HiPCO SWCNTs, (c) Laser SWCNTs, and (d) Arc SWCNTs
parameters, for instance, the content of metals, the bundle diameter of CNTs, the number of walls, and the crystallinity of CNTs (Arepalli et al., 2004). It is interesting to note the strong correlation between the sample purity (or catalyst amount) and the burning temperature for all the SWCNTs in Fig. 3.2a–d. The unusual endothermic burning behavior was observed at the sample typically with high metal content, which can be seen in the CVD SWCNTs in Fig. 3.2a. The Laser SWCNTs in Fig. 3.2c revealed two peaks in the differential TGA. The first peak could be identified as the burning temperature of amorphous carbons (Shi et al., 2000; Sadana et al., 2005). The second peak could be regarded as the SWCNT peak but the burning temperature was low mainly due to the presence of large amount of catalysts (∼ 10 wt%). The burning temperature can be also related to the number of defects on the CNT walls.

The SWCNT powders were also characterized by Raman spectroscopy. Figure 3.3 shows the Raman shift of the samples at excitation energies of 514 nm (2.41 eV) and 633 nm (1.96 eV). The metallicity of each sample can be determined from the radial breathing modes (RBMs). For a given laser excitation energy, the SWCNTs whose allowed transition energies between van Hove singularities are in agreement with the excitation energy, will be excited to produce the Raman signal. This is known as the resonant Raman spectroscopy. Since the positions of van Hove singularities are dependent specifically on the diameter and chirality,
the metallicity of the excited SWCNTs can be determined thoroughly (Rao et al., 1997; Jorio et al., 2001; Kuzmany et al., 2001). At 514 nm, the Laser and the Arc samples revealed only the semiconducting nanotubes. On the other hand, the CVD and the HiPCO samples contained both metallic and semiconducting nanotubes. The metallic component of SWCNTs was further evidenced by the presence of long tail at lower energy side in the $G$-band, i.e., the Fano line representing the metallic contribution (Brown et al., 2001a). At 633 nm, the Laser and the Arc samples picked up mostly metallic SWCNTs, whereas the CVD sample retained mostly semiconducting SWCNTs and the HiPCO sample contained both metallic and semiconducting SWCNTs. In addition to RBMs and $G$-band, the $D$-band was also present in all samples. $D$-band near $1320\;\text{cm}^{-1}$ originates in general from the presence of defects, although its exact origin was not certain (Brown et al., 2001b).

The intensity of $D$-band indicates the amount of defects on the nanotube walls. Another intriguing parameter is the intensity of the $G'$-band. The $G'$-band is the second-order Raman signal, which is the first overtone of the $D$-band. Geng et al. (2007) found that $G'$-band is governed by the metallicity of the CNTs, i.e., the intensity of $G'$-band is directly proportional to the metallic composition of nanotubes. At 514 nm, the Arc and Laser samples revealed relatively small intensities, because they contained mostly semiconducting nanotubes, as shown in Fig. 3.3a. On the other hand, the CVD and HiPCO samples contained a certain portion of metallic composition, therefore yielding the large intensities of the $G'$-band. At 633 nm, similar trend of the changes in the intensity of $G'$-band was observed. The intensity of $G'$-band increased with increasing metallic composition in each sample.

3.3.2 Material Quality Factor for SWCNTs

We obtained several parameters of the SWCNTs used in our study. Figure 3.4 presents the summary of the material parameters of the SWCNT samples. The average diameters of each sample were determined from the TEM. Arc SWCNTs had the largest average diameter among other types, as shown in Fig. 3.4a. Figure 3.4b shows the burning temperature changing with the purity of SWCNTs. More impurities such as transition metals and carbonaceous particles indicate degradation of conductivity. Figure 3.4c presents the intensity ratio of $D$-band to $G$-band and $G'$-band to $G$-band at excitation energies of 514 and 633 nm, respectively. The presence of defects is represented in terms of the relative intensity ratio of $D$-band to $G$-band. This leads to lower the electrical conductivity of metallic CNTs. The abundance of metallic components is represented by the intensity ratio of $G'$-band to $G$-band. More metallic nanotubes results in higher conductivity of the materials.

The band gap of semiconducting nanotubes is inversely proportional to the diameter, $E_g = 2\, a_{cc} \gamma_0 / D$ (eV), where $a_{cc}$ is 0.142 nm and $\gamma_0$ is an empirical tight-binding parameter taken as 2.9 eV (Dresselhaus et al., 2005). The conductivity of SWCNTs can generally be simply expressed as

$$\sigma = ne\mu_n + pe\mu_p$$

(3.1)
where $n$ and $p$ are the $n$-type (electrons) and $p$-type (holes) carrier concentrations, respectively, and $\mu_n$ and $\mu_p$ are the respective electron and hole mobility. The mobility is dominated by a succession of random scattering from collisions with lattice atoms, impurity atoms, and other scattering centers. The intrinsic carrier concentration decreases exponentially with band gap, $n_i = n_o \exp(-E_g/2k_BT)$, where $k_B$ and $T$ are the Boltzmann constant and temperature of the system, respectively. The $p$-type and $n$-type nanotube carrier concentrations are, $p = n_i \exp[(E_i - E_f)/k_BT]$, and $n = n_i \exp[(E_f - E_i)/k_BT]$, where the intrinsic Fermi level $E_i$ is frequently used as a reference level when the extrinsic semiconductors are discussed with a Fermi level of $E_f$. The conductivity is proportional to the carrier concentration, $\sigma \sim \exp(-E_g/2k_BT)\exp[(E_i - E_f)/k_BT]$ for semiconducting nanotubes. For intrinsic semiconducting nanotubes, $E_i = E_f$. On the other hand, in metallic nanotubes, $\pi$ and $\pi^*$ overlap at the Fermi level, i.e., metallic nanotubes are always metallic independent of the diameters. Nevertheless, Delaney et al. (1998) had suggested that the nanotubes are usually bundled and a pseudogap of $\sim 0.1 \text{ eV}$
is open due to the tube-tube interaction. This pseudogap is small compared to the direct bandgap of semiconductors with diameters of $1 \sim 1.4 \text{ nm}$ corresponding to bandgaps of $0.7 \sim 1.0 \text{ eV}$ (An and Lee [2006]). The pseudogap in metallic SWCNT bundles is inversely proportional to the tube diameter via $E_{pg} \approx 0.105/D$ (eV) after fitting to the observed values [Ouyang et al. [2001]]. Thus, the conductivity of metallic nanotubes reveals the similar diameter dependence to semiconducting ones, $\sigma \sim \exp(-E_{pg}/2k_B T)$.

As we described before, the intensity of the $G'$-band is a measure of the abundance of metallic nanotubes. Therefore we propose this concept in quantifying the metallicity of nanotubes. It is also noted in our samples that the intensity of the $G'$-band is strongly correlated to the intensity of metallic peaks in RBMs. Despite the abundance of metallicity, the presence of defects on the nanotube walls that may act as scattering centers degrades the conductivity of the SWCNT network. The intensity of the $D$-band indicates the amount of defects on the nanotube walls. Therefore, an appropriate parameter to express conductivity of nanotubes for SWCNT films is the intensity ratio, $G'$-band/$D$-band. High abundance of metallicity and few defects on the nanotube walls will be desired for high conductivity of the SWCNT films.

From these analyses, it may be useful to extract a practical parameter as a figure of merit to evaluate the metallicity of SWCNTs. The purity affects the conductivity. The diameter contributes to the conductivity via bandgap described in the previous paragraph. More defects reduce the mean free path of carriers and decrease the mobility of carriers in nanotubes. The intensity ratio of $G'$-band/$D$-band may represent the mobility of the carriers. The conductivity is proportional to the metallicity of nanotubes and inversely proportional to the number of scattering centers or defects. Here, we define an effective material quality factor $Q_m$ that governs the conductivity of SWCNTs

$$Q_m = P \times \frac{-E_g}{e^{2k_B T}} \times e^{\frac{E_i - E_f}{k_B T}} \times \sum I_S + e^{\frac{-E_{pg}}{2k_B T}} \times \sum I_M$$

(3.2)

where $E_g = 0.82/D$ (eV) and $E_{pg} = 0.105/D$ (eV) from the previous paragraph, $D$ (nm) is the average diameter of individual SWCNTs and $P$ is the purity of the sample. The intensity ratio of $G'/D$ was averaged over the excitation energies of Raman spectroscopy for each metallic and semiconducting nanotubes. Here $I_S (I_M)$ is defined as

$$I_S (I_M) = I_{G'/D} \times \frac{A_S (A_M)}{A_M + A_S}$$

(3.3)

where $A_S (A_M)$ is the area intensity of semiconducting (metallic) peaks of RBMs from Raman shift in Fig. 3.3. The first exponential term in Eq. (3.2) represents the carrier concentration and the second exponential term represents the mobility that changes with doping effect from semiconducting nanotubes. The second term represents the contribution from metallic nanotubes. Thus this formula resembles the conductivity of Eq. (3.1). Only two wavelengths were used in our study but it
Fig. 3.5 The material quality factor of SWCNTs defined by Eq. (3.2) in the text

seemed satisfactory to explain the TCF performance in terms of $Q_m$. The abundance of metallic nanotubes is implicitly expressed in the intensity ratio of $G'/D$. Since the exponent of metallic nanotubes is much greater than that of semiconducting nanotubes with typical diameters of $1 \sim 2.0 \text{ nm}$, the first term can be negligible in Eq. (3.2) in intrinsic nanotubes when $E_i \approx E_f$. The semiconducting nanotubes generally are sensitive to the environment invoking a doping effect. In such cases, the Fermi level can be shifted and the first term may not be negligible. Although the pseudogap of metallic nanotubes can be affected by a doping effect (Kwon et al., 1998; Zhu et al., 2005), we didn’t consider it in Eq. (3.2), since it is relatively small in comparison to that of semiconducting nanotubes. We calculated the material quality factor $Q_m$ in case of $E_i \approx E_f$. Figure 3.5 shows the material quality factor $Q_m$ of the four SWCNTs in our study. From this point of view, the Arc sample was presumably the best sample that provided the highest conductivity than other types of SWCNTs considered in this work, as can be compared from Fig. 3.5.

3.3.3 Film Characteristics of SWCNTs

Once the prepared SWCNT powder was dispersed in deionized water with SDS, as described in experiment, this solution was sprayed onto the PET film to form thin SWCNT TCFs. Figure 3.6 presents the characteristic curves for sheet resistance-transmittance. For a direct comparison, at 80% of transmittance, the Arc TCFs showed the lowest sheet resistance of about 160 $\Omega$/sq, whereas the CVD TCFs showed the highest sheet resistance. From the material point of view, as discussed in the previous paragraph, this general trend of the film performance seemed to be quite understandable.

We calculated the sheet conductance of TCFs at transmittance of 70 and 80% from Fig. 3.6 and plot as a function of material quality factor. Figure 3.7 shows the sheet conductance of TCFs at a transmittance of 70 and 80% as a function of the material quality factor $Q_m$. We clearly observed a direct correlation between the sheet conductance and the material quality factor. The sheet conductance reveals a linear relationship with the material quality factor. Although this empirical formula
Fig. 3.6 Characteristic curves of sheet resistance-transmittance for various SWCNT TCFs. Each curve contains several data points from TCFs with different number of spray times. Transmittance at 550 nm was selected for comparison. SWCNTs were dispersed in deionized water with SDS.

is not rigorous, it can provide at least a means of estimating material quality that governs the conductivity of the SWCNT TCFs. For instance, large diameter, higher purity, less defects (lower intensity of D-band), and more metallic nanotubes (higher intensity of G′-band) will give better conductivity of the SWCNT TCF. From this point of view, the Arc TCF is the best sample providing the highest conductivity in comparison to TCFs made by other types of SWCNTs considered in this work, as can be seen from Fig. 3.6. However, it may be conjectured that different optimization conditions for dispersion and film preparation may change the TCF properties. In spite of such a possibility, the argument for the material quality dependence described above still holds true. The trend of the change in sheet conductance is similar at different transmittance regions, although the slopes are different. This suggests that our definition of the effective material parameter is quite understandable from a material point of view to describe the TCF performance.

The film morphologies of the SWCNT network of TCFs are presented in Fig. 3.8. All other processing parameters except types of SWCNTs were kept constant through the TCFs preparation process. It is noted that the film morphologies of the CVD and the HiPCO TCFs were significantly different from those of the Laser and the Arc samples. The circular spots were visible in the CVD and the HiPCO samples, as can be seen in Fig. 3.8a–b. These are the remaining SDS surfactants in the film in spite of the repeated washing process. This resulted presumably from

Fig. 3.7 The sheet conductance changes as a function of the material quality factor at different transmittance of 70 and 80%
the stronger binding of surfactants with defects on the SWCNT walls that were hardly removable in the current process compared to the Laser and the Arc samples. Another important feature is the sparseness and networking capability of the CNT bundles. The Laser and the Arc films revealed low CNT density but better network formation by an entanglement of the SWCNT bundles. On the other hand, the CNT density in the CVD and the HiPCO films was high but with relatively less degree of entanglement. As a consequence, the transmittance in the CVD and the HiPCO films was significantly dropped at high density of the CVD and HiPCO films. From the SWCNT density and networking capability of the CNT films, the Arc sample again seemed to be the best material for TCFs among these samples we studied in this work.

3.4 Conclusion

In summary, the flexible TCFs with various types of SWCNTs have been investigated by using spray method. The characteristics of TCFs were analyzed by both the material quality factors and the film quality factors. We extracted all the material parameters of SWCNT powders such as diameter, purity and burning temperature, $D$-band and $G'$-band in Raman spectra. We found that $G'$-band represented well the metallicity of SWCNTs. We defined the material quality factor that dominated the conductivity of SWCNTs by using the diameter, purity, and the average of intensity ratio of $G'$-band to $D$-band. The sparseness of the SWCNT network and the degree of entanglement in the film were also important film parameters to determine the conductivity of the film. By taking account of all these associated effects, we were able to provide an explanation of the SWCNT film performance. A further improvement in the film performance could be possible by choosing highly conductive CNTs evaluated by material quality factor and by enhancing the degree
of dispersion of CNTs in various solvents. In addition, with enhancing the film properties, it will make the CNT-based TCFs possible for flexible display applications.

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References


