Improved Conductivity by Effective Wetting of Single Walled Carbon Nanotubes Film

S. Manivannan, Je Hwang Ryu, Il Ok Jeong, Jin Jang and Kyu Chang Park*
Department of Information Display and Advanced Display Research Center,
Kyung Hee University, Seoul 130-701, Korea
**TEL:82-2-961-9447, e-mail: kyupark@khu.ac.kr*

Keywords : Carbon nanotubes, transparent conducting films, post treatment

Abstract

We describe the fabrication of transparent conducting single-walled carbon nanotubes (SWCNTs) film on flexible substrate following the conventional spin coating method. The fabricated film was post treated with diluted acid solution and its electrical and optical characterizations were performed. The electrical conductivity of SWCNTs film was enhanced and the film was found to be attached strongly with substrate after the post treatment.

1. Introduction

Due to the unique properties, single-walled carbon nanotubes (SWCNTs) appear ideal for a wide range of current and future applications in display, optoelectronics and photovoltaics [1,2]. Transparent conducting oxides (TCOs) such as indium tin oxide (ITO) are commonly used to realize such applications. ITO often requires high processing temperatures and can be very brittle, making it a poor candidate for thermally sensitive substrates [3]. SWCNTs can overcome many of these shortcomings. One of the challenges is to develop flexible and durable transparent electrodes using SWCNTs thin films that have high conductivity [4]. They can be prepared by a variety of techniques including vacuum filtration, spray, inkjet and dip coating [5-7]. Nevertheless, each technique has its own merits and demerits. The performance of the nanotubes film strongly related to purity, diameter, defects, metallicity and degree of dispersion. The commercially available SWNTs reach purity 60-90 % irrespective of production and purification methods. The remaining impurities/debris severely affects the nanotube/film performance. An approach could be useful to reach maximum purity without affecting the pristine structure of the tubes. Therefore, a method to be developed that allows for practical implementation of SWCNTs coatings which is scalable, less expensive and suitable for practical applications. In this paper, we report fabrication of SWCNTs film using spin coating method and purification by post treatment process.

2. Experimental

The commercial arc discharge SWCNTs (Iljin Nanotech.) were used in the present investigation after purification by dry oxidation and acid treatment process. The dispersion of purified nanotubes was accomplished in 1,2-dichlorobenzene (DCB) without using any surfactants/polymers. Ultrasonication was carried out to debundle and disperse the nanotubes in DCB. The nanotube dispersed solution was used to fabricate the films on flexible polyether sulphone (PES) by spin coating method. The spin coated films were backed at 80 ^{0}C for 3 min. The fabricated films were further immersed in diluted nitric acid (HNO_3) solution for 60 min followed by washing in deionized water (DI) and dried at room temperature. The films were characterized structurally by Raman and scanning electron microscope (SEM). The optical transmittance of the fabricated films was measured using UV-Vis-NIR spectrophotometer. The sheet resistance was measured using four point probe.

3. Results and discussion

Figure 1 shows the DCB dispersed SWCNTs after ultrasonic process. It is clear from the Fig.1 that the dispersed solution contains mixture of bundles and dispersed SWCNTs. The ultrasonic treatment in

DCB leads to a debundling while DCB form negatively charged molecules around the nanotubes. The repulsive forces caused by the electrical charges lead to a stable suspension. The main advantage of this method was debundling and dispersion of nanotubes without using surfactants or polymers. Thus, the pristine structure of SWCNTs was retained after the debundling process. Though the nanotubes were purified, impurities are still embedded on the films. These impurities were severely affecting the properties of nanotubes and so the conductivity of the films was limited. The removal of impurities and bundles through centrifugation process leads the wastage of nanotubes that increases the production cost of the films and so the as such SWCNTs dispersed DCB solution was used to fabricate the films.

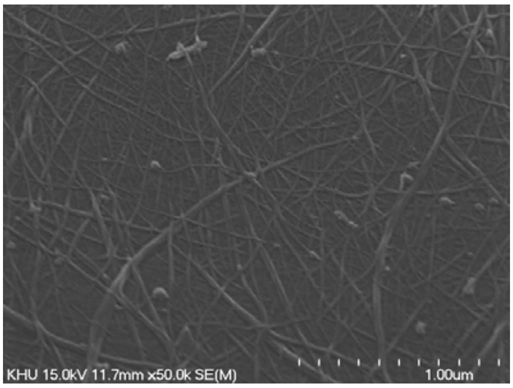

Fig. 1. SEM image of SWCNTs in DCB consists of bundles and dispersed nanotubes.

The relationship between the optical transmittance and sheet resistance in a wide range of film thickness in comparison with as coated and post treated SWCNTs film on flexible PES is shown in Figure 2. From Fig.2, one can notice that initially the sheet resistance decreases nearly 6 times after the post treatment and the decreasing rate become lower while increasing thickness of the films. The sheet resistance versus transmittance curve appears almost linear after the post treatment. In the present investigation, we reached average sheet resistance 100 Ω/□ for ~80 % transmittance at 550 nm after the 60 min post treatment. Thus, the present work met the requirements of touch screen applications at where 500 Ω/□ for 85 % transmittance is sufficient. The wavelength dependence of optical transmittance of a nanotube network of transmittance 84% at 550nm is shown in Figure 3. The as coated and 60 min acid treated films were transparent in the whole visible and infrared region. In addition, no remarkable change in the transmittance was observed after the post treatment process. In contrast to ITO, for which a peak of the transparency was observed at 550 nm, the nanotube network retains high transparency towards the near IR part of the electromagnetic spectrum. One should note that in contrast to ITO, where transmittance is mainly determined by the reflectance of the film, transmittance <100% for SWCNTs films is due mainly to absorbance in the film.

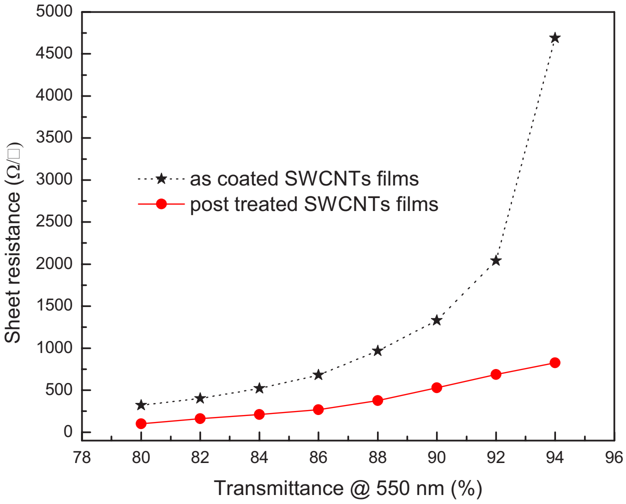

Fig. 2. Transmittance versus sheet resistance of as coated and post treated SWCNTs film on PES.

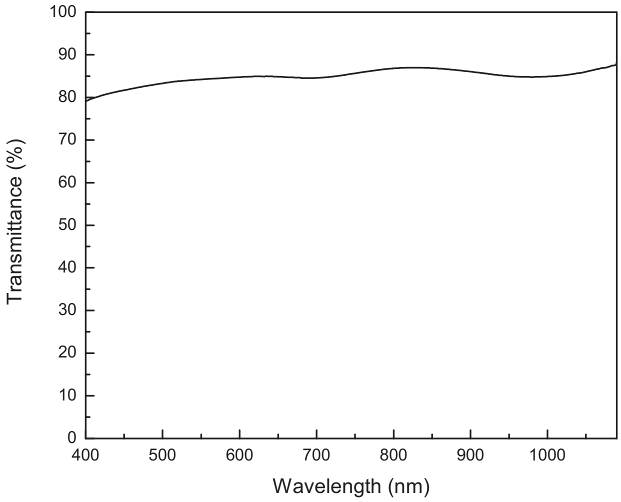

Fig. 3. Optical transmittance of post treated SWCNTs film on PES.

Figure 4 shows room temperature Raman spectra of raw (4a) and 60 min post treated (4b)

SWCNTs films. The first order allowed band with sub structure in the region ~1550-1650 cm^{-1} known as single high frequency band (G-band) signature for highly crystalline sp^2 carbon material. The effects on the high frequency Raman spectra of carbon nanotubes due to wall disorder and possible chemical functionalization during the purification and post treatment processes can be anticipated. There chemical changes are expected to broaden the structure and to increase the integrated intensity and width of the disorder induced band (D-band) normally appears around 1350 cm^{-1}. Interestingly, no significant increase in the I(G)/I(D) intensity ratio was observed after the post treatment, favors no structural damage on the tubes during this treatment. Similarly, the SWCNTs exhibit a unique, low frequency, first order Raman scattering feature identified with the radial breathing mode (RBM) of the tube wall. The observed Raman spectra in the present investigation look like a Gaussian diameter distribution centered on a mean diameter of 1.3 nm. This is mere indication for our sample composed of all the possible (n,m) nanotubes that usually exhibit a Gaussian diameter distribution around some mean diameter.

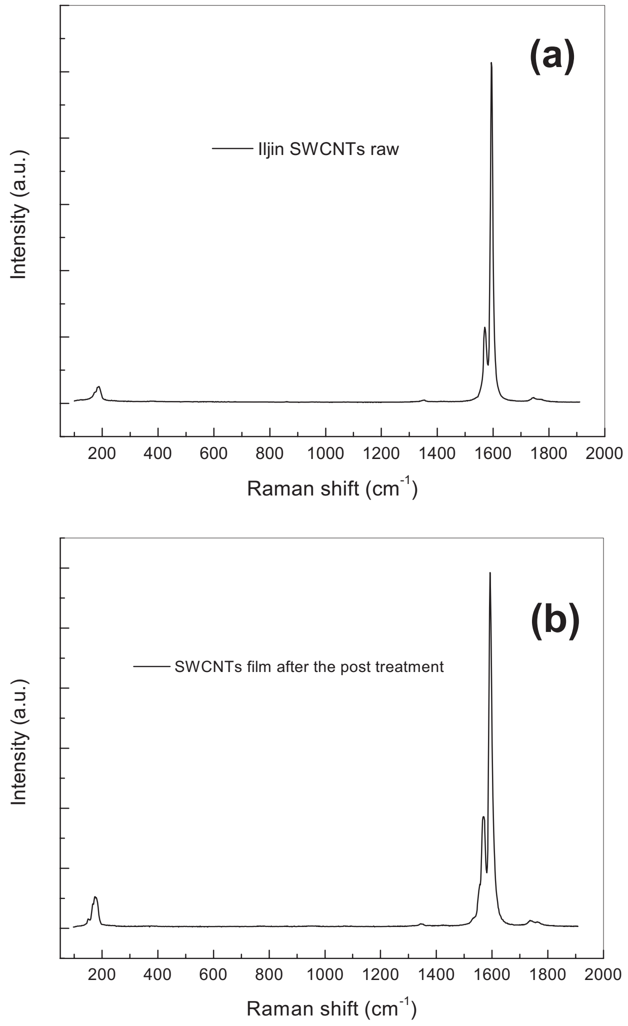

Fig. 4. RBM, D and G bands of Raman spectra of Iljin raw (a) and post treated (b) SWCNTs.

To understand the effect of post treatment, the films were further analyzed by SEM. The SEM images of as coated and post treated films are shown in Figure 5. It is clear from Fig. 5 (a) (indicated in circles), some of the nanotubes were protruded from the substrates to a length of a few nanometer to micrometer. This limits the density of nanotubes on the given surface; in turn significantly increases the

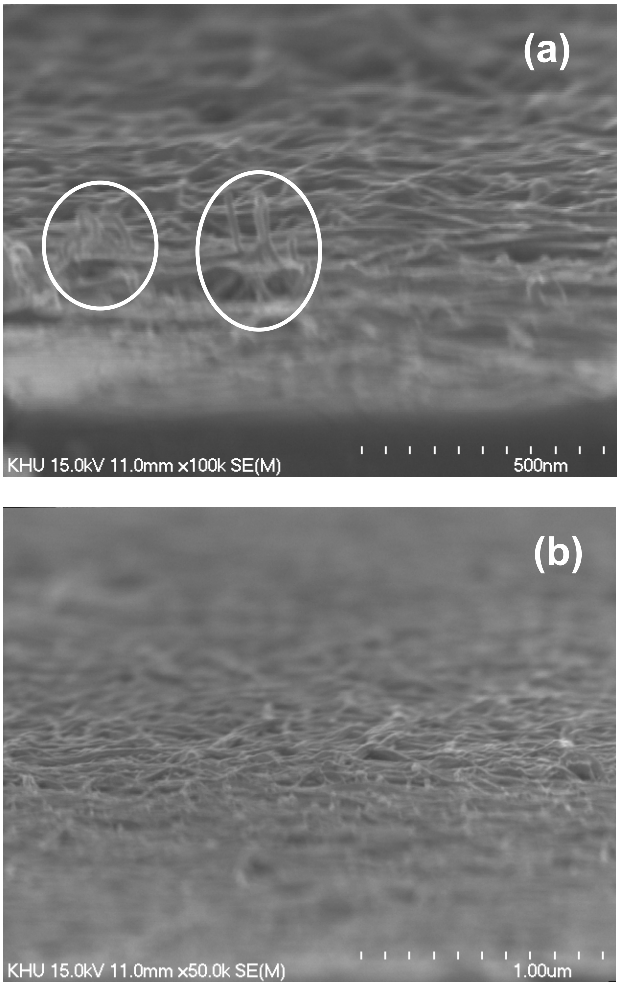

Fig. 5. Side view of SEM images of as coated (a) and 60 min post treated (b) SWCNTs film.

sheet resistance by restricting the nanotubes contact in the network. In addition this will leads to increase the surface roughness and instability of the film. This difficulty was overcome after the 60 min of post treatment (Fig. 5b). The effective wetting by acid, softened the tubes and hence, protruded tubes were flattened, increasing the smoothness by densification of the films. Another interesting effect of post treatment is the digestion of impurities embedded on the film. More importantly, post treated films remained strongly adherent to the PES surface.

4. Summary

We demonstrated a method for preparing SWCNTs film from the solution of debundled arc discharged SWCNTs. The Raman spectral analysis indicates that the purification and post treatment process is a physical rather than a chemical process, since there is no evidence of damage and covalent bonds. The acid solution rapidly wets the nanotubes that densified on the surface and easily etches the impurities on the film. These two contributions enhances the conductivity without sacrificing its optical transparency and stability. Our method can be suitable for large size applications in the next generation flexible electronics.

5. References

1. 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).
2. S. Manivannan, Il Ok Jeong, Je Hwang Ryu, Chang Seok Lee, Ki Seo Kim, Jin Jang and Kyu Chang Park, *J. Mater. Sci: Mater Electron.* (In press)
3. L. Hu, G. Gruner, J. Gong, C-J. Kim and B. Hornbostel, *Appl. Phys. Lett.* **90,** 093124 (2007).
4. M.H. Andrew Ng, L.T. Hartadi, H. Tan and C.H. Patrick Poa, *Nanotechnolgy,* **19**, 205703 (2008).
5. N. Saran, K. Parikh, D-S. Suh, E. Munoz, H. Kolla, S. K. Manohar, *J. Am. Chem. Soc.* **126,** 4462 (2004).
6. Y. Zhou, L. Hu, G. Gruner, *Appl. Phys. Lett.* **88**, 123109 (2006).
7. D.Zhang, K. Ryu, X. Liu, E. Polikarpow, J. Ly, M.E.Tompson, C. Zhou, *Nano Lett.* **6,** 1880 (2006).