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Xiao, Gaozhi; Tao, Ye; Lu, Jianping; Zhang, Zhiyi

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Highly Transparent and Conductive Carbon Nanotube Coatings Deposited on Flexible Polymer Substrate by Solution Method

Gaozhi Xiao*, Ye Tao, Jianping Lu, and Zhiyi Zhang

Institute for Microstructural Science, National Research Council Canada

Abstract- Transparent single-walled carbon nanotubes (SWCNT) based flexible conductive coatings have found great application potentials in flexible displays and solar cells. In this paper we report a simple method for the fabrication of this type of conductive coatings. By using plasma treatment of the flexible polymer substrates, the fabrication of SWCNT flexible coating can be easily achieved through a simple dip coating process. Initial results show that one-dip yields a sheet resistance of $128 \Omega/\square$ and film transmission of more than 90% at the wavelength of 550 nm, while two-dip produces a coating with a sheet resistance of $75 \Omega/\square$ and transmission of more than 80% at the wavelength of 550 nm. The performances achieved are comparable to those of the ITO coatings and significantly better than those reported in the literature for the SWCNT coatings produced by using similar methods.

I. INTRODUCTION

Flexible and transparent electrodes are the basis of flexible displays and solar cells, in which transparent conductive coatings are deposited on flexible polymer substrates. Currently, indium tin oxide (ITO) conductive coatings are the preferred choice as it provides good electrical conductivity and high transparency in the visible region. However, ITO coatings deposited on flexible substrate, such as polyethylene terephthalate (PET), tend to lose its conductivity after mechanical strain [1-3]. For example, Na and coworkers [1] reported that the resistance of ITO on PET increased by ~ 40 times after ~ 2500 bending cycles at a radius of ~ 8 mm. On the other hand, carbon nanotube (CNT) conductive coatings have shown great potential in addressing this issue [4,5].

Many techniques have been studied for the fabrication of transparent CNT conductive coatings on polymer substrates [4, 6], Andrade and coworkers [6] compared the electrical properties of transparent CNT networks prepared through four commercially viable solution coating processes, i.e. dip-coating, spray-coating, vacuum filtration and electrophoretic deposition. Their results show that the CNT coatings prepared by dip coating give a much smoother surface as compared to that prepared by spraying. The CNT coating prepared by dip coating also gives the lowest surface electrical resistance for a given transparency ($\sim 186 \Omega/\square$ at $\sim 86\%$ transparency at the

wavelength of 550 nm). Nevertheless, the authors also found that the dip coating process is very tedious and time consuming. It needs multiple dipping cycles to achieve the expected performance.

In this paper, we report an efficient dip coating process for the fabrication of transparent SWCNT conductive coatings on polymer substrates. By treating the flexible polymer substrates using air plasma followed by a rinsing in 3-aminopropyltrimethoxysilane water solution, one or two dip coating processes will produce a highly transparent and conductive SWCNTs based coatings on the polymer substrates.

II. RESULTS AND DISCUSSIONS

The flexible polymer substrates used in this study were commercially-available polyethylene terephthalate (PET) films from DuPont with the trade name of Mylar.

SWCNT (commercial products from the Chinese Academy of Sciences) water solutions were prepared with the help of magnetic stir and sonication. Surfactant Triton x-100 was added to assist the dispersion of SWCNT in water. The solutions were then purified by centrifuge treatment for the purpose of removing the particles and impurities.

As a precondition for properly coating a substrate using solution method, the substrates need to have a very good wettability for the solution. In other words, the solution is capable of spreading on the substrate easily. Studies have found that PET films are relatively hydrophobic and have a poor wettability for water solutions. This probably explains why dip coat CNT on PET surface is tedious and time consuming, as found by ref. 4 and 6. In addition, to form a good bonding, strong physical/chemical interactions are required between the coating and the substrate. Dissimilar materials tend to have weak bonding between them due to their incapability of forming these types of interactions. This also explains the difficulty in dip coating PET directly with CNT water solution. Surface promoters, such as silanes, have been found very effective in improving the bonding between different types of materials. However, as discussed above, the PET surface is hydrophobic, while the silane solution tends to be hydrophilic. It is very difficult to achieve a uniform silane treatment for PET substrate. In this work, we have used air plasma to render the PET surface hydrophilic. Water contact angle measurement confirmed this. Before the treatment, the water contact angle of the solvent cleaned PET is 72 degree, air

*Contacting Author: Gaozhi Xiao is with the Institute for Microstructural Science, National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada (phone: 1-613-991-6159; e-mail: george.xiao@nrc-cnrc.gc.ca)

plasma treatment lower the value to 26 degree. Then we rinsed the plasma modified PET in 3- aminopropyltrimethoxysilane water solution. X-ray photoelectron spectroscopy (XPS) was used to characterize the treatment effects. Fig. 1 shows the O_{1s} spectrum of the solvent cleaned PET surface. As it shows, the O_{1s} spectrum consists of a doublet and a satellite peak at the higher binding energy, which correspond to the O-C (531.80 eV), O=C component (533.39 eV) in the PET structure and the $\pi - \pi^*$ shake-ups (535.22 eV and 538.47 eV) induced by the phenyl ring. Fig. 2 presents the O_{1s} spectrum of the PET after both air plasma treatment and APTMS rinsing. In this spectrum, only C-O groups exists on the PET surface indicating the fully coverage of the PET surface by APTMS.

The dip-coating of SWCNTs was conducted in a fume hood using a home-built dip-coater. One dip coating cycle including the following steps: Firstly, the treated PET films were immersed in the SWCNT solution for 10 seconds and then withdrawn at a speed of 0.5 cm/min; secondly, the coated samples were baked in a Fisher isotherm oven at the temperature of 110 °C for 5 minutes; thirdly, the baked samples were immersed in HNO_3 for 15 seconds and washed by tap water; finally, the samples were blow dried in air. The whole dipping cycle can be repeated depending on the needs.

Fig. 1 O_{1s} spectrum of solvent cleaned PET surface

Fig. 3 O_{1s} spectrum of solvent cleaned, air plasma treated, and then APTMS treated PET

The sheet resistance of the solution prepared samples was measured using a four-point probe method. Each datum

reported is the average of at least five measurements at different spots with a minimum of 5 mm distance between them.

Several types of SWCNT water solutions were prepared and studied. Fig. 3 shows the transmission spectra of two of the dip coated samples. Sample A is dip coated once. It has a sheet resistance of $\sim 128 \Omega/\square$ and film transparency of more than 90% at the wavelength of 550 nm. Sample B is dip coated twice. It has a sheet resistance of $\sim 75 \Omega/\square$ and film transparency of more than 80% at the wavelength of 550 nm. These results are significantly better than those reported in the literature [4, 6].

Figure 3 Transmission spectra of SWCNT films dip coated on PET surfaces

A: One dip; B: Two dips

III CONCLUSION

A very efficient solution fabrication method for SWCNT conductive coating has been developed. The performances obtained are comparable to those of the ITO coatings and significantly better than those obtained by similar methods.

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