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Fabricating Multi-Walled Carbon nanotube based Thin Films without using surfactant

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Abstract

Thin films of acid-treated multi-walled carbon nanotube (MWCNTs) are fabricated on glass substrate by spin coating technique. For this purpose, CNTs are refluxed in the presence of sulfuric and nitric acids with a ratio of 3:1, for 30 minutes. Acid-treated MWCNTs are dispersed into ethanol with a ratio of 1mg CNTs into 1ml ethanol. Since the adhesion of the carbon nanotubes to the glass substrate was week, in order to improve their adhesion, the substrate was functionalized by a 3-aminopropyltriethoxysilane (APTES) binder. Electrical sheet resistance and transmittance were measured using a four-probe technique and Uv-Visisble spectrophotometer at 550 nm in wavelength respectively. It was observed by post-annealing of the films at 285 ºC for 24 hours, their electrical sheet resistance was improved. The ratio of DC-bulk conductivity to optical conductivity which is accounted as a figure of merit of the film was 37 which is acceptable for transparent and conductive films (TCFs).

Keywords: acid-treated; thin films; figure of merit

1. Introduction

Transparent and conductive thin films (TCFs) are one of the great achievements in the investigation of electronic devices such as thin film electronic Hu Y. et. al. (2004) solar cells Unalan H.E. et. al. (2006) and touch screen panels Sun X. et. al. (1996), Li M. et. al. (2003). Indium tin oxide (ITO) films are the basic element for TCFs due to their higher conductivity and higher transparency Sethi S. et. al. (2009), Zhang Li. et. al. (2009). However, using the mentioned materials has many drawbacks such as their limitations when applied in flexible substrate films causing a small strain and reducing the films' electrical performance. Another drawback of ITO is the processing temperature for this material which is high and the films produced by this nanomaterial are brittle. ITO is also, the tremendous demand for its application has caused ITO shortages due to its high application Zhou Y. et. al. (2006), Rowell M.W. et. al. (2006). Carbon nanotube thin films can overcome many of these drawbacks and have a high conductivity and transparency Gomathi A. et. al. (2005). The most important benefit of using carbon nanotube thin

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films is that there is a coating possibility for different substrates and different techniques Joong T.H. et. al. (2008), Joong T.H. et. al. (2009), Hu L. et. al. (2004). The low conductivity of CNT thin films is attributed to the large tube-tube contact resistance between CNTs.

MWCNTs	Multi-Walled Carbon Nanotubes
ITO	Indium Tin Oxide
TCFs	Transparent and Conductive Thin Films
DC-Bulk	Direct Current Bulk Conductivity
CVD	Chemical Vapor Deposition
LED	Light-Emitting Diode

In this study, we fabricated MWCNTs thin films without using surfactant by spin coating techniques on glass substrate and received an acceptable figure of merit in films which was 37 for DC-bulk conductivity to optical conductivity ratio which is acceptable in comparison with CNTs fabricated with different methods. The relation between T, R_s and $\sigma_{Op}/\sigma_{DC,B}$ is given by:

$$T = \left(1 + \frac{Z_0}{2R_s}\frac{\sigma_{op}}{\sigma_{DC.B}}\right)^{-2} \qquad (1)$$

Where Z_0 is the free space impedance (377Ω), σ_{op} is the optical conductivity and $\sigma_{DC,B}$ is the bulk DC conductivity. For a thin film, DC conductivity is thickness-dependent and is proportional to t^n De S. et al (2007), where *t* is the film thickness and *n* is the percolation exponent. De et al. using a simple model have shown that there is another relation between T and R_s of transparent conductors in percolated regime in which the conductivity is thickness-dependent as De S. et al (2007):

$$T = \left(1 + \frac{1}{\Pi}\left(\frac{Z_0}{R_s}\right)^{\frac{1}{1+n}}\right)^{-2} \qquad (2)$$

Π is a dimensionless parameter called the *percolative figure of merit* and its higher values mean higher *T* and lower R_s.

2. Materials and methods

CVD synthesized pristine MWCNTs with a length of 5-15 μm and diameters of less than 10 nm were purchased (Shenzhen Co., China). Commercial round glasses 20 mm in diameter were also used as substrate. Purification and functionalization of the MWCNTs were carried out into a mixture of concentrated sulfuric and nitric acids (95% H_2SO_4, 65% HNO_3; 3:1). Details of acid treatment have been described elsewhere Farbod M. et. al. (2011). In order to have better adhesion between carbon nanotubes and the glass substrates, a 3-aminopropyltriehtoxysilane (APTES) solution was used to modify the substrate's surface. One mg of MWCNTs was dispersed into 1 ml of ethanol by an ultrasonic bath (22 kHz, 100 W) for 15 minutes. The suspension was then centrifuged for 30 minutes to remove the possible particles and large bundles from the suspension. The spin coating method was employed as a fast technique to prepare the films. A final speed of 4900 rpm was chosen. The films were then annealed at 285 ºC for 24 hours. A field emission scanning electron microscope (FESEM: MIRA, TESCAN- Czech Republic) was used to observe the surface morphology of MWCNTs films and to measure the films' thickness. To do so, the glass substrates were tilted in order to have a better view for imaging. Sheet resistance of the films was measured by a 4-point probe technique at room temperature and their optical transmittance by means of a UV-Vis spectrophotometer (Cintra 101, GBC - Australia).

3. Results and discussion

The SEM images of films, shown in Fig. 1, were prepared using 30 min. refluxing time and a typical 135 nm thin film on glass substrate. Fig. 2 shows a circuit set up to light an LED with a battery, using 30 min. refluxed CNTs films with various thicknesses in series with a battery and an LED.

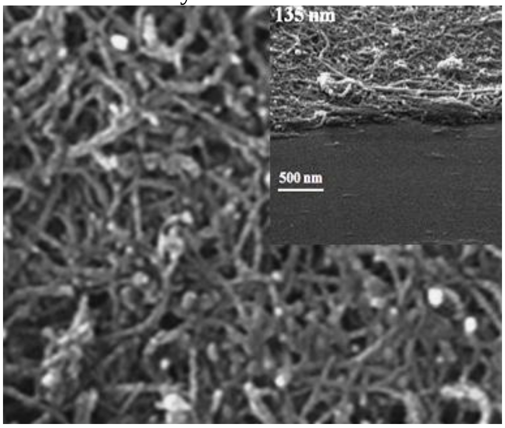

Fig. 1. Typical SEM images of films prepared using MWCNTs. The inset shows the films' thickness.

Fig. 2. Transparency of the films with circuit set up to light an LED, using the films in series with a battery.

Fig. 3 shows the optical transmittance of the films preparing CNTs with different thicknesses. As can be observed, the transmittance increases with decreasing the thickness for all the films. In order to describe the figures' differences, the transmittances of the films at 550 nm were plotted versus their thickness and are shown in Fig. 4. It is clear from this figure that by increasing the films' thicknesses, their transmittance decreases.

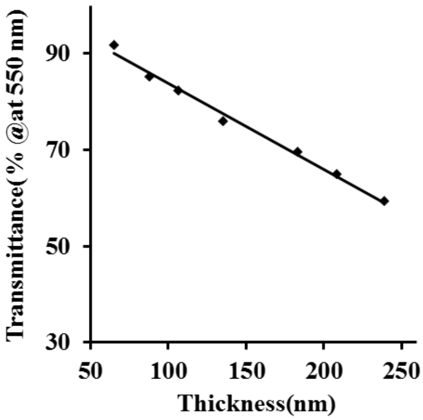

Fig. 3. Transmittance versus thickness for the films prepared using different refluxed time CNTs.

The sheet resistance of the films was plotted versus their thickness and shown in Fig. 4. As can be seen from this figure, the sheet resistance reduces with increasing the thickness exponentially. Also, the sheet resistance shows no significant thickness dependency when the thickness is higher than 300 nm. The films were annealed at 285 ºC after being spin-coated. We found that the post-heat treatment has a remarkable influence on the reduction of sheet resistance and the improvement of the films' optical transmittance. It seems that before annealing, the potential barrier between the CNTs junctions is high and the free carriers are impeded thereby making the electrical conductivity poor. By post annealing, the contacts and fusion between the CNTs are improved, resulting in the reduction of sheet resistance.

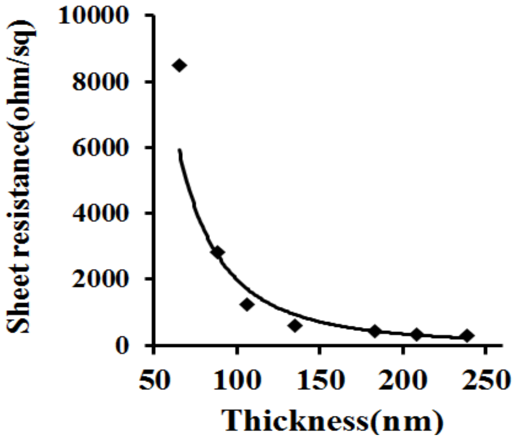

Fig. 4. Sheet resistance versus films thickness for films prepared using refluxed CNTs.

Figure 5 shows the plot of the optical transmittance at 550 nm versus sheet resistance of the films prepared using CNTs with different lengths. As it is expected, the films with higher transparency typically show higher sheet resistance. It is desirable to have films with high transparency and low sheet resistance. From the figure it is clear to observe that the transparency of the films with the same sheet resistance depends on the length of CNTs and that the films prepared using 30 min. refluxed CNTs show higher transparency. It seems that the settlement of CNTs on the substrate during film coating is arranged in a manner that shorter CNTs allow for less light transmission.

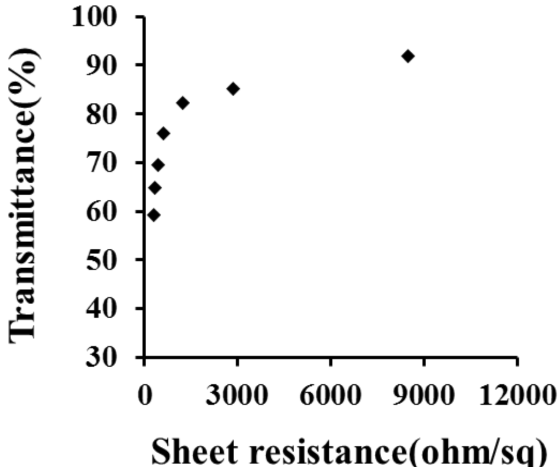

Fig. 5. Optical transmittance at 550 nm versus sheet resistance for the films prepared using refluxed CNTs.

Based on our data, the $\sigma_{DC,B} / \sigma_{Op}$ ratios were calculated using equation (1). In order to calculate the films percolative figure of merite (Π) and n the percolation exponent, equation (2) using log-log plot of the $(T^{-0.5} -1)$ versus R_s was employed. The calculated parameters are listed in Table 1.

Table 1. Values of $\sigma_{DC,B} / \sigma_{Op}$, Π and n found from fitting in curves of $(T^{-0.5} - 1)$ versus R_s for different films.

Refluxed time (min)	$\sigma_{DC,B}/\sigma_{op}$	σ_{op}(S/m)	n	Π
30	37	7427.1	0.9	4.5

The results show that the $\sigma_{DC,B} / \sigma_{Op}$ is acceptable for films which are made by carbon nanotubes thin films.

4. Conclusion

In the present study, carbon nanotube thin films with different thicknesses were fabricated and their sheet resistance and optical transmittance were measured. It was observed that the sheet resistance and optical transmittance of MWCNTs films were extremely dependent on the CNTs thickness. The results showed that the films prepared using 30 minutes refluxed CNTs with longer lengths reveal higher conductivity and transmittance. The figure of merit was 37 for the films prepared using 30min. refluxed CNTs respectively. It means a percolation conducting path can be achieved by longer length carbon nanotubes at lower thickness and therefore higher transmittance.

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