Surface conductivity of aligned carbon nanotubes in silica gel

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Abstract

Aligned carbon nanotubes (CNT) (individual diameter ~ 15nm) have been grown within a silica gel film using catalytic nickel nanoparticles. The surface electrical resistivity shows a variable range hopping mechanism to be operative between them.

Keywords: Carbon nanotube; Hopping; Gel.
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1. Introduction

Carbon nanotubes (CNT) have attracted considerable attention since their discovery [1]. This is due to their unique physical properties and many potential applications. CNT have been investigated for possible application as a field – emission electron source [2-6]. Use of CNT in nanoelectronics has been explored [7-10]. Various methods have been adopted to synthesize carbon nanotubes. Some of them are arc discharge [11, 12], laser vaporization [13], pyrolysis [14], plasma-enhanced [15] or thermal chemical vapour deposition (CVD) [16, 17]. The approach has been to use nanometer-sized metal catalysts on a substrate on which CNT have been grown. An oxidized silicon substrate with a thin film of iron on it has been used for this purpose [18]. Also catalytic chemical vapour disposition (CCVD) method has been considered to be economic route for synthesis of large scale CNT [19].

Here, growth of aligned carbon nanotube bundles is described. We have employed a silica gel film with nickel nanoparticles dispersed in it. Bundled CNT have been grown within the film. The individual nanotube has diameter about 15nm. Transmission electron micrographs indicate that these nanotubes are aligned. The surface electrical resistivity measured by placing electrodes on the gel film surface shows a variable range hopping mechanism to be operative.

2. Method of Analysis

The points in Figure 5 represent the experimental data and the lines are the theoretical fits to the equation describing the variable range hopping conduction [20].
where, $\rho_o$ is the pre-exponential factor and $T_o$ is given by

$$T_o = \frac{8b_c\chi^3}{fN(E_F)k}$$  \hspace{1cm} (2)$$

$b_c \sim 1.5$, $\chi$ is the tunneling constant and for graphite can be taken as $1\text{A}^{0.4}$, $f \sim 1.0$, $N(E_F)$ is the density of states for CNT at the Fermi level and $k$ the Boltzmann constant. The values of $N(E_F)$ extracted from the slopes of the two straight lines shown in Fig. 5 are $1.8 \times 10^{12}$ and $2.8 \times 10^{13}$ eV$^{-1}$ cc$^{-1}$ for specimens 1 and 2 respectively. It is evident that this value increases by an order of magnitude when the reduction treatment is increased. This is consistent with the increase in the number of carbon nanotubes as pointed out earlier. It is envisaged that in the present case variable range hopping takes place between nanotube bundles (interbundle hopping). Therefore, evident that in the present specimens of gel-derived films containing nickel nanoparticles it has been possible to grow carbon nanotubes on the film surface. It is believed that the nanometer – sized pores within the gel provide the channels through which the carbon nanotubes grow.

3. Experimental Procedure

The target composition for the gel film was 90 SiO$_2$, 10 NiO (in mole %). In preparing the solution, 5 ml of distilled water was added to 4.162 ml of tetraethylorthosilicate. Another solution was prepared by adding 5 ml of distilled water to 0.4819 gm of NiCl$_2$, 6H$_2$O. The two solutions were mixed and 30 ml of ethyl alcohol was poured into the mixture. The pH of the latter was maintained at $\sim 4.0$ by adding 0.1 ml of 11N nitric acid. The resulting solution was stirred for 3 hours. A Corning 4059 glass plate with dimension 2.5 cm x 1 cm x 3 mm was cleaned with acetone and diluted HF for 30 seconds and dipped into the resulting solution. The films produced in this dip-coating process were dried in an oven at a temperature of 353K. Then the films were first subjected to a reduction treatment in hydrogen at temperatures 823K and 923K for $1/2$ hour to produce nanometer – sized nickel particles in the gel matrix. After this the films were introduced inside a furnace raised to a temperature of 1073K through which acetylene gas mixed with dry nitrogen gas ($C_2H_2 : N_2 = 1 : 10$) was passed at a flow rate of 700 c.c./min for 15 minutes. In this process aligned bundled carbon nanotubes were grown on nanometer-sized nickel nanoparticles. The specimens subjected to reduction treatments at 823K and 923K prior to carbon nanotube growth within them will be referred to subsequently as specimens 1 and 2 respectively.

4. Results and Discussion

The structural characteristics of the carbon nanotubes grown were investigated by a JEM 200 CX transmission electron microscope. Surface electrical resistivity of the film was measured by applying two silver paint electrodes (supplied by Acheson Colloiden, B.V. Holland) of width $\sim 8$ mm separated by $\sim 1$ mm on the film surface. The resistance of the sample was measured by a 617 Keithley Electrometer over the temperature range 100K to 300K.
Figure 1: Transmission electron micrograph for specimen 1.

Figure 1 is the transmission electron micrograph for the specimen, which was subjected to a reduction treatment at 823K for ½ hr. before carbon nanotubes were grown on it by cracking acetylene (C₂H₂) over it at 1073K for ¼ hr. Figure 2 is the electron diffraction pattern obtained from Figure 1. Table 1 summarizes the values of interplanar spacings computed from the diameters of the diffraction rings and compares these with standard ASTM data. It

Table 1: Comparison of interplanar spacings d_{hkl} as obtained from Figure 2 with ASTM data

<table>
<thead>
<tr>
<th>Observed d_{hkl} (nm)</th>
<th>ASTM data</th>
<th>Graphite d_{hkl} (nm)</th>
<th>Nickel d_{hkl} (nm)</th>
<th>Nickel Oxide d_{hkl} (nm)</th>
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is seen that the observed interplanar spacings confirm the presence of graphite (the major phase), nickel and nickel oxide (as minor phases). We have also taken transmission electron micrograph (Figure 3) at higher magnification, which shows the diameter of individual CNT is about 15nm. These results are typical of all the samples studied here. In Figure 4 the variation of resistivity as a function of inverse temperature is shown for specimens 1 and 2 investigated here. It is seen from the Figure 4 that the surface resistivity of the carbon nanotube – silica gel composite decreases as the reduction temperature increases. Such a change of resistivity is ascribed to the fact that the number of carbon nanotubes per unit area on the film surface increases as the density of the nickel nanoparticles increases. The subsequent discussion will elucidate this point further.

The electrical resistivity behavior in the present series of samples has been analysed on the basis of a variable range hopping model because of the localized states provided by the carbon nanotubes [21]. The Variable Range Hopping theory is based on the idea that charges are localized but can every now and then jump (“hop”) to another localized state. Actually the presence of small electrical barriers (because of intertube contacts or structural defects insight CNTs itself) give rise to localization effects. Figure 5 shows the variation of
log resistivity as a function of $T^{-\frac{1}{4}}$ for the two samples for which the electrical data were presented in Figure 4. The straight line behaviour for both the plots is remarkable.

Figure 5: Variation of resistivity as a function of $T^{-\frac{1}{4}}$ for different specimens.

\[ \Delta \text{ Specimen no. 1} \quad \square \text{ Specimen no. 2} \]

5. Conclusion

In summary, aligned bundled carbon nanotubes with diameters about 15nm have been grown within a silica gel matrix. These aligned nanotubes are shown by transmission electron micrographs. Surface electrical resistivity is found to be controlled by a variable range hopping mechanism between the nanotubes. This simple method of producing aligned carbon nanotubes can be exploited to make field-emission electron source.

References

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