Electrical characterization of multiwalled carbon nanotubes synthesized by DC- plasma enhanced chemical vapor deposition technique

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Abstract   Thermoelectric and electrical conductivity properties of multiwalled carbon nanotubes deposited by plasma enhanced chemcal vapor deposition with acetylene as precursor using Ni as a catalyst on Si substrates have been studied in detail The substrate temperature has been varied from 750 – 850°C It was found that the thermoelectric power of the MWCNT is positive over the whole temperature range, and increases with increasing the deposition temperature and showed p-type conduction in the films Room-temperature Seebeck coefficients were found in the range 11 12 to 31 24 µVK⁻¹, for films deposited with different substrate temperature X-ray diffraction studies confirmed the graphitic phase of carbon nanotubes Transmission electron microscopy study showed the diameter of the carbon nanotubes lying in the range 15-20 nm The room temperature electrical conductivity (σ_{RT}) of the carbon nanotubes increased with increase of the substrate temperature, as usual for semiconductors and the highest room temperature electrical conductivity obtained was 4 07 × 10⁻¹ S cm⁻¹ for the sample deposited at 850 °C substrate temperature

Keywords · Carbon nanotubes; Thermoelectric properties ; p-type conductivity

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1. Introduction

Carbon nanotubes continue to attract much research interest due to their remarkable mechanical and electrical properties and promising applications. The carbon nanotubes consist of concentric tubes of graphene sheets. Different groups showed that the nanotubes have metallic or semiconducting properties depending on their diameter and chirality [1]. Nanotubes have been widely used for many applications, such as field emission electron guns [2], optical communication device [3], scanning microscope probe tips [4], electronic circuits [5], and nanowires [6]. The most common production techniques for carbon

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nanotubes are hydrogen arc discharge, thermal chemical vapor deposition, hot filament-assisted sputtering, RF magnetron sputtering and Plasma enhanced chemical vapor deposition (PECVD). We have chosen plasma enhanced chemical vapor deposition (PECVD) for the production of carbon nanotube, because it is a high yield and controllable method for production carbon nanotubes with mass production. We have used Ni as a catalyst for the formation of carbon nanotubes, because carbon nanotubes formed on Ni are more crystalline than those formed using other catalyst [7]. In this paper we report the synthesis of carbon nanotubes *via* DC-PECVD technique. Thermoelectric and other electrical properties of the films have been studied. X-ray diffraction patterns and transmission electron microscope (TEM) were used to characterize the structure of the films.

2. Experimental details

For the deposition of Ni catalyst in thin film form by dc sputtering process we have used a Ni plate of thickness ~ 1 mm with a dimameter 2.5 cm (with purity 99.99%, Aldrich). The substrates were 10 × 10 mm^2 cleaned Si (400) wafer. The sputtering was done at a pressure 0.2 mbar sending argon as a sputtering gas. The deposition was made for 7 minutes at room temperature with an inter-electrode distance 1.6 cm. For sputtering, we maintained high voltage 2.0 KV and corresponding current density was 19.5 mA cm^{-2} After deposition of the catalyzed film, the sample was immediately transferred to the CVD chamber where the synthesis of nanotubes was performed. The deposition chamber was initially evacuated by a standard rotary and diffusion pumps arrangement upto a base pressure of 10^{-6} mbar. The silicon substrate was placed on a Molybdenum substrate holder, which could be directly heated. When the chamber pressure attained 10^{-6} mbar, the Mo substrate holder was started to heating by sending current thorugh it. The substrate temperature was measured by a disappearing filament type Pyrometer (PYROPTO, IT65). Acetylene (C$_2$H$_2$) gas was used in PECVD process as a precursor of carbon. Acetylene (C$_2$H$_2$) gas was allowed to flow maintaining the CVD chamber pressure 50 mbar. Deposition was performed at 2.0 kV dc supply with corresponding current density 25 mA cm^{-2} for 30 min. Substrate temperature was varied from 750 to 850°C for different set of samples.

3. Results and discussion

3.1 Nanostructural studies and X-ray diffraction :

The nanostructure of the films was studied by a transmission electron microscope (TEM, JEM-2010, JEOL, JAPAN). The micrographs of multiwalled carbon nanotubes have been shown in Figure 1. From figure it was found that the diameter of the carbon nanotubes decreases with increase the substrate temperature. *In our experiment the Ni catalyst particles were prepared in a separate DC sputtering unit as described in the experimental section. Then these Ni particle-coated Si substrates were placed in the CVD chamber. The chances of coalescence of the Ni nanoparticles will depend on two factors : on their proximity and also on the rate of substrate temperature increment. In our case the nano Ni particles were well dispersed and the substrate temperature was increased very quickly*

to the desired value (we used Mo thin plate as a heater, hence very large current could be made to flow very quickly) Hence in our experiment the Ni nanoparticles could not form bigger particles by coalescence With the increase of substrate temperature the rate of diffusion of the carbon precursor through the metal catalyst increased, that led to smaller diameter but larger length.

Figure 1 HRTEM micrograph of the MWCNTs film deposited at (a) 800 °C and (b) 850 °C

X-ray diffraction pattern was recorded by a X-ray diffractometer (Bruker D8 Advance) in 2θ range 20° – 80° using Cu Kα radiation of wavelength λ = 0 15406 nm The films deposited on Si substrates showed crystalline structure as shown in Figure 2 The XRD spectrum showed various peaks of carbon nanotubes due to diffraction from (022), (100), (004) and (110) planes The interplanner spacing (3 40 Å, 2 12 Å, 1 71Å and 1 23Å) obtained form XRD peaks are well matched with the standard reported data [8] From the X ray diffraction of carbon nanotubes (as shown in Figure 2), the (100) and (110) peaks have been observed at 42 62° and 77 45° respectiely and the inter-planar spacing (d_{100} = 2 12 Å and D_{110} = 1 23) is little smaller than that of graphite (d_{100} = 2 13 Å and d_{110} = 1 23), which indicates the carbon nanotubes and graphite have similar structures [9]
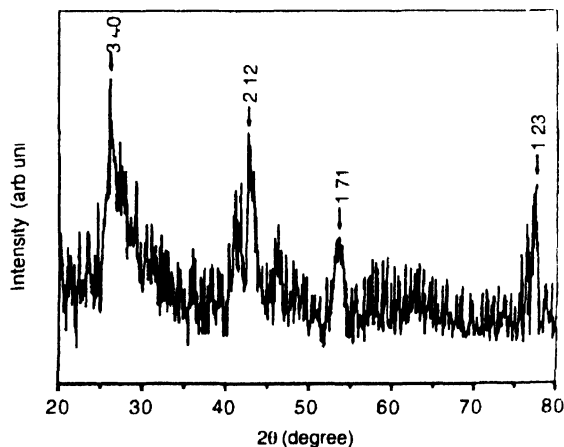

Figure 2. X-ray diffraction pattern of the carbon nanotube film deposited at 850°C

3.2 Electrical measurements :

The electrical conductivity was measured by usual four-probe technique using Keithley electrometer (model 6514) to measure the current. All contacts were made by silver paste which showed ohmic characteristics over a wide range of voltages and temperatures The electrical conductivity of the films can be expressed by the standard relation as follows :

$$\sigma = \sigma_0 \exp\left[-\frac{E_a}{kT}\right]$$

where σ_0 is a temperature independent factor, E_a is the activation energy of the material For p-type semiconductor, this is the energy difference between the acceptor level and the top of the valence band. Therefore, the slope of the plot of $\ln\sigma$ vs 1000/T would carry the information of the activation energy of the material as shown in Figure 3. The electrical conductivity (σ) of the films deposited with different substrate temperature has been measured at temperature (T) ranging from 300 K to 450 K. The conductivities of the films increase with the increase of temperature as usual for semiconductor. An increase in the room-temperature conductivity (σ_{RT}) was observed with the increase in deposition temperature (t) of the films. (For example, films with t = 750, 800 and 850 °C, σ_{RT} = 5.29 × 10³, 1.64 × 10³, 1.64 ×10⁴ and 4.07 × 10⁴ S cm⁻¹). From the slope of the graph we calculate the activation energy (Ea). It was found that after 375K the activation energies (E_{aa}) for the CNT films varied from 0.096 to 0.056 eV and below 375K activation energies (E_{ab})varied from 0.776 to 0.513 eV. The lowest activation energy was obtained for the sample deposited at 850 °C substrate temperature. The two types of activation energies, arises in two different temperature range, are due to two different acceptor levels generated during growth of the materials. To activate the carriers in these accetpor levels of our MWCNT thin films, two different energies are required.
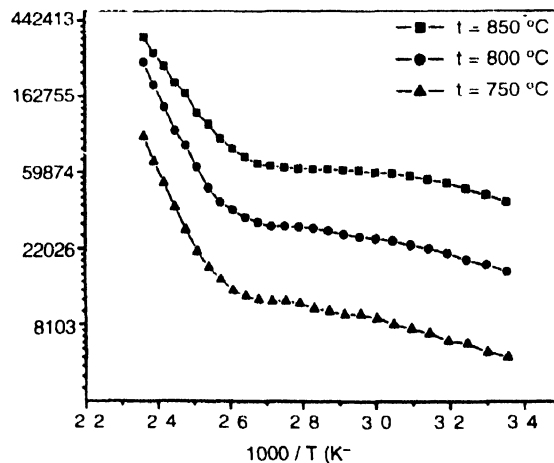
Figure 3. In σ vs 1/T plots of the CNT thin films for different substrate temperature (t).

The thermoelectric power of the films has been measured keeping the cold junction at room temperature (300 K) and the temperature of the hot junction was varied from 300 to 450 K. The seebeck coefficients of the films were calculated from the slope of the plots of thermo-emf (E) *vs.* difference of temperature (T) between the hot and cold junctions. Figure 4 shows the seebeck coefficient (S) *versus* 1000/T plots for the MWCNT thin films for different substrate temperature during deposition. Seebeck coefficients increased with the increase of substrate temperature during deposition of the carbon nanotubes thin films. The values of room temperature seebeck coefficients for the films lying in the range 11 12 to 31.24 μVK^{-1} for different deposition temperature. Room temperature seebeck coefficient is 31.24 μVK^{-1} for 850°C substrate temperature, which is higher than at TEP of CNT reported by Tian *et al* [10] and always positive. This may imply that the majority carriers in the nanotube should be P-type, and hole carriers are dominant. This result is in good agreement with the Hall coefficient measurement reported by Song *et al* [11] where the observed Hall coefficients are positive over entire temperature range. From the well-known Mott relation it is known that the Seebeck coefficient *S* depends on the density of state function at the Fermi level [12]. Now with the decrease of diameter of the *MWCNT*, the surface to volume ratio increased and hence the density of defect state increased near the Fermi level. The Seebeck coefficient for the *CNT* films deposited at higher temperatrue increased as in this case diameter of the *MWCNT* decreased.
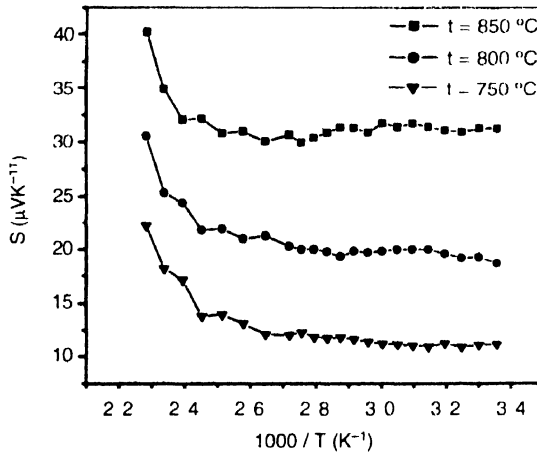

Figure 4. Seebeck coefficient (S) *vs.* 1000/*T* of MWCNTs thin films for different substrate temperature during deposition (t)

4. Conclusion

MWCNTs in the thin films form have been successfully synthesized on Si substrates *via* PECVD using Ni as a catalyst. X-ray diffraction patterns have confirmed the graphitic phase of carbon nanotubes. TEM studies showed that the CNTs are multiwalled. The diameter of the carbon nanotubes lies in the range 15-20 nm. The room temperature conductivity of the carbon nanotubes increased with increase of the substrate temperature, as usual for semiconductors and the highest room temperature conductivity obtained was

4.07 ×10^4 S cm^{-1} for the sample deposited at 850 °C substrate temperature. Thermoelectric measurement of the carbon nanotubes thin films, showed considerable high value of room-temperature seebeck coefficients ranging from 11.12 to 31.24 μVK^{-1}, for different substrate temperature during deposition of the films with p-type conductivity. This study shows the MWCNTs may become a useful candidate for thermoelectric applications.

Acknowledgment

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