Enhancing electrical properties of carbon nanotubes thin films by silicon incorporation

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Abstract. Silicon incorporated carbon nanotube (Si-CNTs) thin films was prepared by radio frequency plasma enhanced chemical vapor deposition technique. Tetraethyl orthosilicate solution was used for incorporation of silicon in CNTs thin films. Energy dispersive X-ray analysis shows that the silicon atomic percentage was varied from 0 % to 6.1 %. The chemical binding energies of carbon and silicon were analyzed from X-ray photoelectron spectroscopy data. The various peaks at ~531 eV, ~ 285 eV, ~155 eV and ~104 eV was observed in the XPS spectra due to the oxygen, carbon and silicon respectively. Surface morphologies of Si-CNTs thin films have been analyzed by field emission scanning electron microscopy, which reveals that the length of the silicon incorporated carbon nanotubes ~500 nm and corresponding diameter ~80 nm. The room temperature electrical conductivity was increased whereas the activation energy was decreased with the increase of atomic percentage of silicon in Si-CNTs thin films. The room temperature electrical conductivity was increased from 4.3 x 10³ to 7.1 x 10⁴ S cm⁻¹ as the silicon atomic percentage in Si-CNTs thin films increases from 0 to 6.1 % respectively.

Keywords. Carbon nanotubes, RF-PECVD Technique, Silicon incorporation, XPS, Electrical conductivity.

1. Introduction

Nanostructures graphene planes in rolled form are the building block of carbon nanotubes (CNTs). CNTs are composed of one or more closed hollow graphite cylinders, with few hundred nm in diameter and a few microns in length. Generally CNTs are two types; single- walled when the number of graphene sheet is one and multiwalled, if more than one graphene sheet formed tube [1,2]. CNTs have been widely used for many applications, such as device making for optical communication, probe tips for electron microscope, different electronic circuits, water purification, water disinfection, hydrogen storage, field emission electron guns, nanowires, gas sensors, biomedical energy and air purification [3-11]. Depending on the synthesis technique, single walled carbon nanotube and multiwalled carbon nanotubes with different surface structure can be prepared. The various preparation methods and characterizations of CNTs have been reported by various researchers because of their incredible properties and different prime applications in the nanotechnology. The basic procedure for preparation of CNTs are RF magnetron sputtering, solvothermal technique, AC-arc discharge, laser evaporation, Electrolysis, hot filament-assisted sputtering, catalytic chemical vapour deposition (CCVD), electrosprinning and plasma enhanced chemical vapor deposition (PECVD) [11-21]. PECVD technique is one of the best root for the preparation of nanostructured carbon because of high yield and controllable technique for the production of CNTs at lower substrate temperature.
Doping of CNTs is a promising approach to control the electronic structure and is of high technological importance for the practical device manufacturing. Study of doped CNTs useful in understanding the perturbed physical properties caused by the dopants in one-dimensional materials and gives an opportunity to attainment their remarkable properties in innovative and relatively fast growing technology. The opportunity of alternate element such as iron, gold, boron, phosphorus, sulfur and nitrogen doping in CNTs has generated intense interest due to the feasibility of tailoring structural and electronic properties of CNTs by different doping elements [22-29].

In this paper, we have reported the synthesis of Si-CNTs thin films via radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) technique in thin film form. Nanostructure surface morphology characterization was done by field emission scanning electron microscope (FESEM). The details chemical bonding information was analysed by X-ray photoelectron spectroscopy (XPS) data. Temperature dependence electrical conductivities of Si-CNTs thin films were studied for various atomic percentage of silicon in the CNTs thin films. The activation energy was calculated and has explained.

2. Experimental Procedure
2.1. Preparation of silicon incorporated CNTs thin films
Different transition metal such as nickel, iron, cobalt has been used as catalyst in the growth of carbon nanotubes by chemical vapour deposition technique. Nickel (Ni) thin films were deposited on alumina substrates was used as a catalyst for Si-CNTs preparation. The deposition of Ni catalyst thin film on the substrates was done by direct current (DC) sputtering technique. Before starting the deposition of Ni thin films, all alumina substrates were ultrasonically cleaned in methanol for 10 minutes at 30 °C temperature and rinsed thoroughly with double distilled water 2-3 times continuously then soaked with hot air gun. A Ni target of 99.99 % pure was used for DC sputtering technique. The DC sputtering performed at 0.15 mbar chamber pressure using Ar as a sputter gas. During DC sputtering the voltage and current density were 2.5 KV and 20 mA cm\(^{-2}\) respectively. A ~20 nm thick (measured by Inficon make digital thickness monitor Model: SQM-160) Ni catalyst thin film deposited on alumina substrates. After preparation of Ni catalyst thin film, the alumina substrates were kept within the RF-PECVD unit. The RF-PECVD chamber was evacuated with a base pressure of 10\(^{-6}\) mbar. A transformer was used for heating the substrate during Si-CNTs thin films preparation and the temperature of the substrate was maintained at 450 °C. The mass flow controller (MFC) key was used for entering the acetylene (C\(_2\)H\(_2\)) gas into the evacuated chamber with 12 sccm and was maintained the RF-PECVD chamber pressure 1.5 mbar during CNTs thin films growth. The preparation of Si-CNTs thin films has been done at 170 watt RF (13.56 MHz) power for 20 min. The precursor solution for silicon incorporation in CNT thin films made by tetraethyl orthosilicate (TEOS) mixed with methanol with different concentration. The solution was kept in a bubbler and Ar gas (10 sccm) was send to the RF-PECVD unit through the bubbler, which controlled by MFC key. The different concentration of TEOS solution were used for the variation of silicon atomic percentage in Si-CNTs thin films. The complete synthesis parameters for preparation of Si-CNTs thin films are described in table 1.

| Table 1. Synthesis parameters for preparation of Si-CNTs thin films. |
|-------------------------|------------------|
| **Synthesis parameters** | **Corresponding values** |
| Acetylene gas           | 12 sccm          |
| Ar gas                  | 10 sccm          |
| Base pressure           | 10\(^{-6}\) mbar |
| Working pressure        | 1.5 mbar         |
| Substrates used         | Alumina coated with nickel thin film |
| Deposition temperature  | 450 °C           |
| Deposition time         | 20 min.          |
| RF power                | 170 watt         |
2.2. Characterization of Si-CNTs thin films
The nanostructure surface morphology of Si-CNTs thin films were investigated by using a scanning electron microscope (FESEM, JEOL-JSM-6360) and the silicon, carbon composition were measured by energy dispersive X-ray analysis (EDX, Oxford, model-7582). The binding energy of different electronic states of carbon and silicon of the Si-CNTs thin films were analyzed by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer-1257). The hemispherical energy analyzer was used for the XPS spectra analysis. The background correction and analysis of the XPS data were done by Shirley technique. The Mg Kα non-monochromatic X-ray was used as the excitation source with energy 1253.6 eV. The XPS system pressure was ~10⁻⁹ mbar during measurement. A standard four-probe instrument used to study the electrical conductivity measurement of the Si-CNTs thin films with different temperature. To make the ohmic contact for electrical conductivity measurement, gold electrodes were deposited on Si-CNTs thin films by thermal evaporation technique.

3. Results and discussion
3.1. Analysis of composition for Si-CNTs thin films
The atomic percentage of silicon and carbon in the Si-CNTs thin films was analyzed from the EDX spectra. The EDX spectra of the Si-CNTs thin films synthesized on alumina substrate is shown in figure 1. It was observed that the atomic percentage of silicon in the CNTs thin films within range of the concentration of TEOS solution. The atomic percentage of silicon in the Si-CNTs thin films was varied by using different concentration of TEOS solution which shown in In table 2. In EDX spectra, the peak due to carbon, aluminium and oxygen was observed in both pure CNTs and silicon incorporated CNTs thin films, whereas silicon peak was detected for doped CNTs thin films. In the EDX spectra, the peak of the aluminium and oxygen comes from alumina substrate.

![Figure 1. EDX spectra for (a) pure CNTs thin films and (b) silicon incorporated CNTs thin films was prepared using 8 % TEOS solution.](image1)

3.2. Surface morphology studies
The topographical image of Si-CNTs thin films was taken using a FESEM as shown in figure 2. The FESEM image showed the CNTs are randomly oriented on substrate. The length and diameter of the CNTs and Si-CNTs ~ 500 nm and ~ 80 nm respectively.
3.3. XPS analysis

Figure 3(a) and (b) shows the XPS spectra of pure CNT thin films and 6.1 atomic percent Si content CNTs thin films respectively. The XPS spectra of the Si-CNTs thin films shows the different peaks. In the XPS spectra, the peaks at ~531 eV, ~285 eV, ~155 eV and ~104 eV were observed due to O 1s, C 1s, Si 2s and Si 2p respectively [30,31]. The Si core level XPS spectrum was shown in the inset of figure 3(b). Two binding energy peaks corresponding to Si 2s at 104 eV and Si 2p at 155 eV respectively was found in core level spectra, which justify that silicon has been incorporated into the CNTs. XPS is a quite surface sensitive analysis technique. In XPS spectra, the peak at ~531 eV was appeared due to oxygen. In figure 3(a), there is a peak corresponds to oxygen for the pure CNTs thin films synthesized without using of TEOS solution. The oxygen peak in the both XPS spectra confirms that Si-CNTs surface contaminated by oxygen from different sources [32-34].

Figure 3. (a) Full XPS graph of the pure CNT thin films and (b) Si-CNTs thin films with 6.1 atomic percentage silicon content and the Si core level spectra of 6.1 at. % Si content CNF thin films in inset.
3.4. Electrical Conductivity analysis

The well-known equation for the study of electrical conductivity ($\sigma$) of semiconductor thin films is expressed by equation 1 as follows [35]:

$$\sigma = \sigma_0 \exp \left[ -\frac{E_a}{kT} \right]$$ (1)

Where $k$ is Boltzmann constant and its value is $1.38 \times 10^{-23}$ joule/ kelvin, $\sigma_0$ is a temperature independent factor and $E_a$ is the activation energy of the material respectively. The activation energy known as the energy difference between top of the valence band and the acceptor level in case of p-type semiconductor and similarly the energy difference between bottom of the conduction band and the donor level in case of n-type semiconductor respectively. The equation (1) is a straight line equation and the plot between $\ln \sigma$ vs. $1/T$ should be a straight line. The electrical conductivity measurement with the variation of temperature for the Si-CNTs thin films was carried out. Several set of measurements was performed for different silicon content Si-CNTs thin films. The change in the electrical conductivities of Si-CNTs thin films ware observed from the conductivity measurement analysis. The $\ln \sigma$ vs. 1000/T plot for Si-CNTs thin films with different atomic percentage of silicon is shown in figure 4(a). The room temperature electrical conductivity of the Si-CNT thin films was increased from $4.3 \times 10^3$ to $7.1 \times 10^4$ as the silicon atomic percentage in the CNTs thin films increase from 0 to 6.1 respectively as shown in figure 4(b).

![Figure 4](image_url)

**Figure 4.** (a) Temperature dependent electrical conductivity of Si-CNTs thin films for different atomic percent of silicon and (b) variation of room temperature electrical conductivity and activation energy with various atomic percent of silicon in Si-CNTs thin films.

**Table 2.** The room temperature electrical conductivity for Si-CNTs thin films with various atomic percentage silicon as measured by EDX.

| Nominal Si in TEOS solution (at. %) | Si from EDX (at. %) | ($\sigma_{RT}$) S cm$^{-1}$ |
|-----------------------------------|---------------------|-----------------------------|
| 0                                 | 0                   | $4.3 \times 10^3$           |
| 2.5                               | 1.6                 | $9.3 \times 10^3$           |
| 4.0                               | 3.1                 | $1.8 \times 10^4$           |
| 6.0                               | 4.4                 | $3.3 \times 10^4$           |
| 7.5                               | 6.1                 | $7.1 \times 10^4$           |
The increased of temperature, electrical conductivity ($\sigma_{RT}$) of the Si-CNTs thin films was increased, which similar as for semiconductor. The activation energy ($E_a$) for Si-CNTs thin films was calculated from the slope of the graph of ln$\sigma$ vs. 1000/T, which decrease from 0.13 to 0.08 eV as the silicon content in the CNTs thin films increase from 0 to 6.1 atomic percent respectively. The electron transport phenomenon can be explain with the diffusion process [36,37]. There is a barrier potential exits in the doped CNTs, which accountable for the electron transport considering diffusive transport phenomenom. The height of the potential energy barrier is given by equation 2

$$E_{\text{barrier}} = E_F - E_V$$

(2)

where $E_F$ is the Fermi energy of CNTs and $E_V$ is the top energy of valence band. In electron transport, the outer wall of CNTs impact is maximum. As a result of doping in the outer wall of the CNTs, the Fermi level perturbed and reduce the energy gap difference between valence and conduction band [37]. As the barrier height decreases, the large number of electrons smoothly tunnel the potential and helps in conductance compare to the pure CNTs. The diffusive transport mechanism highly influence in the electrical conductivity of Si-CNTs thin films, which was prepared by RF-PECVD technique.

4. Conclusions

Si-CNTs thin films was prepared on alumina substrate by using RF-PECVD technique. The atomic percentage of silicon in the CNTs thin films has been varied from 0 % to 6.1 %, which confirm from EDX analysis. FESEM image showed that the CNTs are randomly oriented and the average length of the Si-CNTs ~500 nm and corresponding diameter ~80 nm. Different peaks were observed in XPS spectra due to carbon, silicon and oxygen respectively. The analysis of silicon core level spectra confirms that silicon has been incorporated into the CNTs. The electrical conductivity of the Si-CNTs thin films was increased with increase of the temperature whereas the activation energy was decreased.

The room temperature electrical conductivity ($\sigma_{RT}$) of Si-CNTs thin films was increased from $4.3 \times 10^3$ to $7.1 \times 10^4$ S cm$^{-1}$ with increase of silicon atomic percentage 0 to 6.1 respectively.

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