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Enhancement of Electrical Property of Carbon Nanotube by Silicon Incorporation

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Abstract*: Silicon incorporated carbon nano tube has been synthesized by radio frequency plasma enhanced chemical vapor deposition technique with acetylene gas. Tetraethyl orthosilicate solution was used for the synthesis of silicon incorporation in the CNT thin films. Energy dispersive X-ray analysis shows that the Si atomic percentage in the CNT thin films varied from 0 % to 3.82 %. The different chemical binding energies of carbon and silicon were analyzed from X-ray photoelectron spectroscopy spectra. In the XPS spectra, the peaks at ~531 eV, ~ 285 eV, ~151 eV and ~100 eV are the contributions from O 1s, C 1s, Si 2s and Si 2p respectively. Nanostructure morphologies of the Si-CNT thin films have been analyzed by field emission scanning electron microscopy. The length of the silicon incorporated carbon nano tubes ~100 nm and corresponding diameter ~20 nm. The increase of atomic percentage of Si in the CNT thin films, room temperature electrical conductivity increases. The electrical conductivity increase from $3.87x10^{3}$ to $4.49x10^{4}$ S cm^{-1} as the silicon atomic percentage in the CNT thin films increases from 0 to 3.82 % respectively. This study showed that the Si-CNTs thin films potentially useful in electrical application of varying its conductivity by changing the Si content independently from other parameters.

Keywords* : Carbon nanotubes; Silicon incorporation; XPS; Electrical conductivity.

I. INTRODUCTION

Nanostructures graphene planes in rolled form are the building block of carbon nanotubes. Carbon nanotubes (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 (SW) [1] when the number of rolled graphene sheet is one and multiwalled (MW) [2] if more than one graphene sheet formed tube. CNTs have been widely used for many applications, such as device making for optical communication, probe tips for electron microscope, different electronic circuits, hydrogen storage, field emission electron guns, nanowires and gas sensors [3-9]. Depending on the preparation method, single walled carbon nanotube (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) with different morphologies can be synthesized. The various synthesis procedure and characterization of SWCNTs and MWCNTs have been performed in details during last few years because of their remarkable properties and different significant applications in the nanotechnology. Doping of CNT is a promising approach to control the electronic structure and is of high technological importance for the practical device manufacturing. Study of doped CNT useful in understanding the perturbed physical properties caused by the dopants in one-dimensional (1D) materials and gives an opportunity to attainment their remarkable properties in innovative and relatively fast growing technology. The opportunity of alternate element such as boron, phosphorus and nitrogen doping in CNTs has generated intense interest due to the feasibility of tailoring structural and electronic properties of carbon nanotubes by different doping elements [10-12]. The basic techniques for synthesis of carbon nanotubes are hydrogen arc discharge, thermal chemical vapor deposition, hot filament-assisted sputtering, RF magnetron sputtering and plasma enhanced chemical vapor deposition (PECVD) [13-17]. Among these techniques, PECVD is a controllable and high yield process for preparation of carbon nanotubes [18] with large production. In this paper we report the synthesis of Si incorporated carbon nanotubes (Si-CNT) via radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) technique in thin film form. Morphological characterization done by field emission scanning electron microscope. The details chemical bonding information studied by X-ray photoelectron spectroscopy spectra. Temperature dependence electrical conductivities of the Si-CNT thin films have been studied for various atomic percentage of silicon in the CNT thin films.

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II. EXPERIMENTAL DETAILS

A. Synthesis of silicon incorporated carbon nanotubes

Different transition metal such as Ni, Fe, Co has been used as catalyst in the growth of carbon nanotubes by chemical vapour deposition technique. The 10 nm thick Ni films were deposited on silicon and alumina substrates used as a catalyst for Si-CNT synthesis. The deposition of Ni catalyst thin film on the substrates were done by direct current (DC) sputtering technique. Hydrofluoric (HF) acid (~ 12 %) was used to remove the silicon oxide layer on silicon substrate.

The etching of Si substrates were done for 4-5 minutes with HF acid solution. Finally, all the silicon and alumina substrates were ultrasonically cleaned in for 10 minutes. A Ni target of 2.0 mm thickness, 5 cm diameter and 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 sputtering the DC voltage and current density was 2.5 KV and 20 mA cm^{-2} respectively. A ~10 nm thick (measured by Inficon make digital thickness monitor Model: SQM-160) Ni catalyst thin film deposited on silicon and alumina substrates by sputtering process. After preparation of Ni catalyst thin film, the silicon and alumina substrates was placed on molybdenum plate within the CVD chamber where the Si-CNTs thin film has been synthesized. The base pressure of the CVD chamber was made 10^{-6} mbar. A secondary transformer was connected with the molybdenum plate for heating the substrate during Si-CNTs thin film deposition. The temperature of the molybdenum plate increased with the increasing current through it. K-type thermocouple was used for measuring the temperature of the Ni coated substrate during Si-CNTs thin film deposition. During synthesis of CNT the substrate temperature was fixed at 650 ^{o}C for different set of experiment. The acetylene (C_2H_2) gas was used for CNT synthesis via RF-PECVD technique with chamber pressure 1.5 mbar. The synthesis of Si-CNT thin films has been done at 180 watt RF (13.56 MHz) power for 30 min. The precursor solution for silicon incorporation in the CNT thin films made by tetraethyl orthosilicate (TEOS) mixed with methanol with different concentration. The solution was kept in a bubbler and Ar gas sent to the CVD chamber via the bubbler. The different concentration of TEOS solution used for the variation of Si atomic percentage in the Si-CNT thin films. Table I. Show the deposition parameter for synthesis of Si-CNT thin films.

Table- I: Deposition parameter for synthesis of Si-CNT thin films

Deposition parameters	Corresponding values
Precursor material	Acetylene (C_2H_2)
Gas pressure	1.5 mbar
Substrates used	Ni catalyzed silicon and alumina
Substrate temperature	650 ^{0}C
Electrode distance	4 cm
RF power	180 watt
Deposition time	30 min.

B. Characterization

The topographical image of Si-CNT thin films taken using a scanning electron microscope (FESEM, JEOL-JSM-6360) and the silicon carbon atomic percentage 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-CNT thin films were analyzed by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer-1257). A standard four-probe instrument used to study the electrical conductivity measurement of the Si-CNT thin films with different temperature. To make the ohmic contact for electrical conductivity measurement, gold electrode deposited on the Si-CNT thin films by thermal evaporation technique.

III. RESULTS AND DISCUSSION

A. Analysis of composition for Si-CNT thin films

The atomic percentage of silicon and carbon in the Si-CNT thin films analyzed with the energy dispersive X-ray (EDX) spectra. The EDX spectra of the Si-CNT thin film synthesized on alumina substrate is shown in Fig.1. It has been observed that the atomic percentage of silicon in the CNT thin films within range of the concentration of TEOS solution. The atomic percentage of silicon in the Si-CNT thin films for different TEOS solution used in the deposition process is shown in In Table II. In the EDX spectra the peak of the aluminium and oxygen comes from alumina substrate.

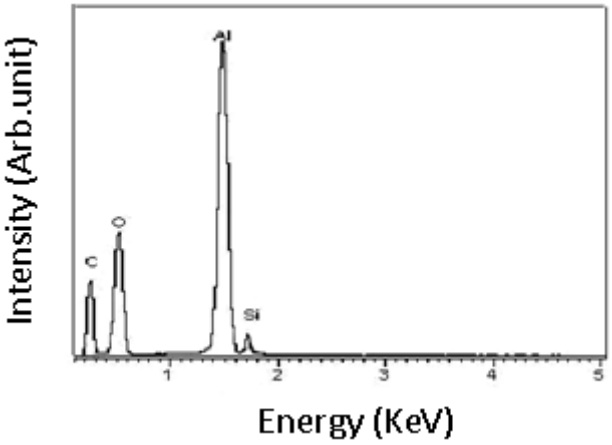

Fig. 1. Energy dispersive X-ray spectra for Si-CNT thin film synthesized using 4 % TEOS solution.

B. Morphology studies

The topographical image of Si-CNT thin films taken using a scanning electron microscope as shown in Fig. 2. The FESEM image showed the carbon nanotube are randomly oriented on substrate. The length and diameter of the silicon incorporated CNTs ~ 100 nm and ~ 20 nm respectively.

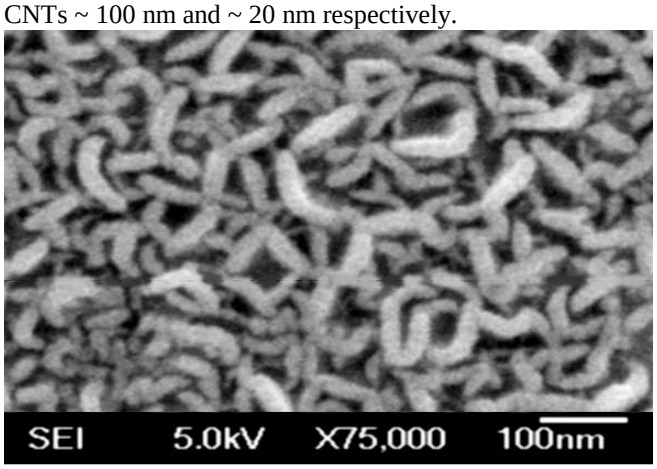

Fig. 2.FESEM micrograph of 3.82 % Silicon incorporated CNT thin films.

C. XPS analysis

The binding energy for different electronic states of carbon and silicon of the Si-CNT thin films were analyzed by X-ray photoelectron spectroscopy spectra.

The hemispherical energy analyzer used for the XPS spectra analysis of the Si-CNT thin films. The analysis and background correction of the XPS data were done by Shirley technique. The Mg Kα non-monochromatic X-ray with energy 1253.6 eV was used as the excitation source. The measurement was done with an anode current 17 mA and at 10 kV. During XPS measurement the system pressure was ~10^{-9} mbar. Fig. 3(a) and (b) shows the XPS spectra of pure CNT and 3.82 atomic percent Si content Si-CNT thin film respectively. The XPS spectra of the Si-CNT thin films shows the different peaks due to carbon, silicon and oxygen respectively. In the XPS spectra, the peaks at ~531 eV, ~ 285 eV, ~151 eV and ~100 eV are the contributions from O 1s, C 1s, Si 2s and Si 2p respectively. XPS is a quite surface sensitive analysis technique. The peak at ~531 eV comes due to oxygen appeared in the XPS spectra. In Fig. 3(a), there is a peak corresponds to oxygen for the pure CNT thin films synthesized without using of TEOS. The oxygen peak in the both XPS spectra confirms that Si-CNT surface contaminated by oxygen from different sources.

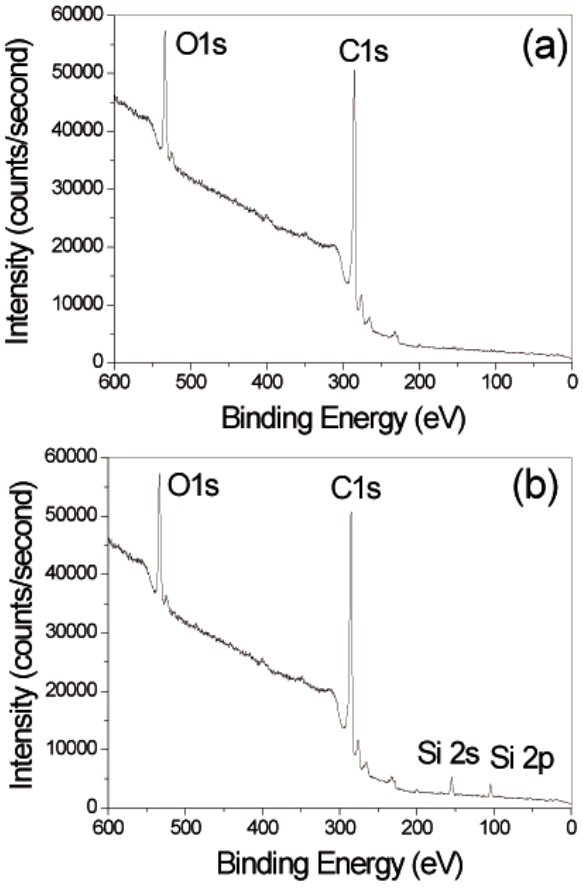

Fig. 3. (a)Full XPS graph of the pure CNT films (b) Si-CNT thin films with 3.82 atomic percentage silicon content.

D. Electrical Conductivity analysis

The standard equation for the analysis of electrical conductivity (σ) of semiconductor thin films is given by [19]:

$$\sigma = \sigma_o \exp[-\frac{E_a}{kT}] \quad (1)$$

σ_0 is a temperature independent factor, *k is* Boltzmann constant and E_a is the activation energy of the material respectively. The activation energy is 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 donner level in case of n-type semiconductor respectively. The equation (1) is a straight line equation and the plot between lnσ vs. 1/T must be a straight line. The activation energy for a material calculated from the slope of the graph of lnσ vs. 1/T. The lnσ vs. 1000/T plot for Si-CNT thin films with different atomic percentage of silicon is shown in Fig. 4.

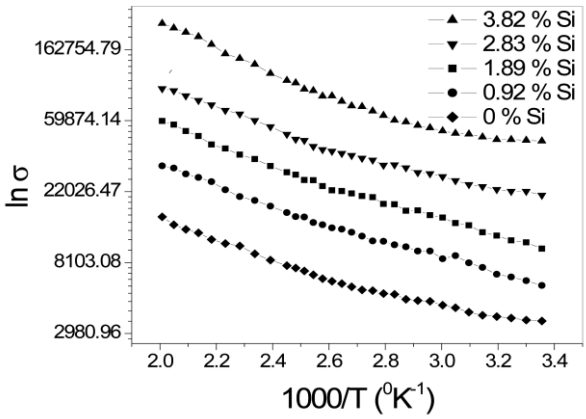

Fig. 4.Temperature dependent conductivity of Si-CNT thin films for different atomic percentage of silicon content.

The electrical conductivity measurement with the variation of temperature for the Si-CNT thin films has been carried out. Several set of measurements have been performed for different silicon content Si-CNT thin films. The measurement showed that there is variation in the electrical conductivities of Si-CNT thin films. The room temperature electrical conductivity of the Si-CNT thin films increased from $3.87x10^3$ to $4.49x10^4$ S cm^{-1} as the silicon atomic percentage in the films increase from 0 to 3.82 respectively.

The increased of temperature, electrical conductivity (σ_{RT}) of the Si-CNT thin films increase which is similar as for semiconductor. From the slope of the graph we calculated the activation energy (E_a). The activation energy (E_a) for the Si-CNT thin films decreased from 0.116 to 0.083 eV as the silicon content in the CNT films increase for 0 to 3.82 percent. The electron transport phenomenon can be explain with the diffusion process. [5,20]. There is a barrier potential exits in the doped carbon nanotube and which is accountable for the electron transport considering diffusive transport phenomenon.

Table-II: The room temperature conductivity for Si-CNT thin films with various Si content as measured by EDX.

Sample name	Nominal % of Si in solution	Si % from EDX	(σ_{RT}) S cm^{-1}
CNT-1	0	0	$4.49x10^4$
CNT-2	1	0.92	$1.86x10^4$
CNT-3	2	1.89	$8.90x10^3$
CNT-4	3	2.83	$5.45x10^3$
CNT-5	4	3.82	$3.87 x10^3$

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The height of the potential energy barrier is given by

$$E_{barrier} = E_F - E_V \qquad (2)$$

where E_F is the Fermi energy of CNT and E_V is the top energy of valence band. In electron transport, the outer wall of CNT impact is maximum. As a result of doping in the outer wall of the CNT, the Fermi level perturbed and reduce the energy gap difference between valence and conduction band [20]. As the barrier height decreases, the large number of electrons smoothly tunnel the potential and helps in conductance compare to the pure CNT. The diffusive transport mechanism highly influence in the electrical conductivity of Si-CNTs thin films synthesizes by RF-PECVD technique. This study reveals that the Si-CNTs thin films potentially useful in electrical application of varying its conductivity by changing the Si content independently from other parameters.

IV. CONCLUSION

Silicon incorporated carbon nanotubes in the thin films form have been synthesized via RF-PECVD technique using Ni as a catalyst. The energy dispersive X-ray analysis (EDX) showed that the atomic percentage of silicon in the CNT thin films has been varied from 0% to 3.82 %. FESEM image showed that the length of the Si-CNTs ~100 nm and corresponding diameter ~20 nm. The XPS spectra of the Si-CNT thin films shows the different peaks due to carbon, silicon and oxygen respectively. The room temperature electrical conductivity (σ_{RT}) of the Si-CNT thin films increased from $3.87x10^3$ to $4.49x10^4$ S cm^{-1} with the increase of silicon atomic percentage 0 to 3.82 respectively. This study showed that the Si-CNTs thin films potentially useful in electrical application of varying its conductivity by changing the Si content independently from other parameters.

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