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# Synthesis and Optical Characterization of Carbon Nanofibers

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***Abstract*: Radio frequency plasma enhanced chemical vapor deposition technique has been used to synthesized graphitic carbon nanofibers thin films. Ni catalyst in thin film form used for the synthesis of carbon nanofibers. The deposition temperature of the substrate has been varied from 500 - 600 $^0$C. The morphology of the CNF thin films changed with the variation of substrate temperature. The graphitic phase of the synthesized carbon nanofibers has confirmed by X-ray diffraction patterns analyses. Field emission scanning electron microscopic studies showed fibrous structure in the films. The length of the carbon nanofibers few micrometers and the diameter range 300-400 nm. The different vibrational modes of carbon nanofibers analyzed using Fourier transformed infrared spectroscopy measurements. Photoluminescence of the carbon nanofibers have also been studied which showed a strong emission peak at 468 nm.***

***Keywords* : Carbon nanofibers; RF-PECVD; XRD; FESEM; FTIR, Photoluminescence.***

## I. INTRODUCTION

Nanocrystalline materials, which can be grown efficiently in different form such as nanoparticles, nanorods, nanobelts, nanowire etc, have attracted much attention due to their novel properties and promising applications. For the assembly of nanodevices, nanostructured materials in one-dimensional form have promising advantage. Nanometer-scale electronics have been predicted to play an important role in device technology. An enormous interest has recently developed in the area of carbon nanostructure materials. Since the discovery of fullerenes [1] and carbon nanotubes/nanofibers (CNTs/CNFs) [2], there has been explosive growth in the field of synthesis and characterization of nanotubes/ nanofibers due to their remarkable properties and potential 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].

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The basic techniques for synthesis of carbon nanotubes/ nanofibers (CNT/CNF) are hydrogen arc discharge, thermal chemical vapor deposition, hot filament-assisted sputtering, RF magnetron sputtering and
plasma enhanced chemical vapor deposition (PECVD) [10-15]. Among these techniques, PECVD is a controllable and high yield process for preparation of CNTs/CNFs [16] with large production.

In this paper we report the synthesis of carbon nanofibers (CNF) via radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) technique in thin film form. X-ray diffraction patterns and field emission scanning electron microscope (FESEM) were used to characterize the structure of deposited CNT thin films. The details chemical bonding information studied by Fourier Infrared Transform spectroscopy (FTIR). Optical analysis of the CNF thin films done by photoluminescence spectra.

## II. EXPERIMENTAL DETAILS

### A. Preparation of Ni catalyst by RF sputtering

Different transition metal such as pure cobalt, iron and nickel has been used as catalyst in the growth of CNF by plasma enhanced chemical vapour deposition technique. The 20 nm thick Ni films were deposited on silicon substrates used as a catalyst for CNF synthesis. The deposition of Ni catalyst thin film on the substrates were done by Radio frequency (RF) sputtering technique. Hydrofluoric (HF) acid (~ 12 %) was used to remove the silicon oxide layer on silicon substrate. The etching of Si substrates was done for 4-5 minutes with HF acid solution. Finally, all the silicon 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 RF sputtering technique. The RF sputtering performed at 0.5 mbar chamber pressure using Ar as a sputtering gas. During sputtering the RF power maintained at 160 Watt. A ~20 nm thick (measured by Inficon make digital thickness monitor Model: SQM-160) Ni catalyst thin film deposited on silicon substrates by RF sputtering process. The deposition parameters for Ni catalyst have been shown in Table-I.

**Table- I: Deposition parameter for preparation of Ni catalyst thin film.**

| Deposition parameters | Corresponding values |
|---|---|
| Sputtering gas | Argon (Ar) |
| Gas pressure | 0.5 mbar |
| Substrates used | Silicon |
| Substrate temperature | 30 $^0$C |
| Electrode distance | 3 cm |
| RF power | 160 watt |
| Deposition time | 15 min. |

### B. Synthesis of carbon nanofiber thin films

After preparation of Ni catalyst thin film, the silicon substrates were placed on substate holder of the RF-PECVD chamber where the CNFs thin film has been synthesized. The base pressure of the RF-PECVD chamber was made $10^{-6}$ mbar by a standard rotary and a turbo molecular pumps arrangement.

During synthesis of CNF thin films, the substrate temperature was fixed at 500 $^{o}$C, 550 $^{o}$C and 600 $^{o}$C respectively for different set of experiment. The acetylene ($C_2H_2$) gas was used for CNF synthesis via RF-PECVD technique with chamber pressure 1.0 mbar. The synthesis of CNF thin films has been done at 150 watt RF (13.56 MHz) power for 25 min. The deposition parameter for synthesis of CNF thin films shown in Table-II.

**Table- II: Deposition parameter for synthesis of CNF thin films**

| Deposition parameters | Corresponding values |
|---|---|
| Precursor material | Acetylene ($C_2H_2$) |
| Gas pressure | 1.0 mbar |
| Substrates used | Ni catalyzed (20 nm thick ) Silicon |
| Substrate temperature | 500 $^{o}$C, 550 $^{o}$C and 600 $^{o}$C |
| Electrode distance | 5 cm |
| RF power | 150 watt |
| Deposition time | 25 min. |

### B. Characterization

An X- ray diffractometer (Bruker D8 Advance) in 2θ range 20 - 80$^{o}$ used for the X-ray diffraction patterns analysis. The Cu $K_\alpha$ radiation of wavelength λ = 0.15406 nm used for R-ray studies. The topographical image of CNF thin films taken using a scanning electron microscope (FESEM, JEOL-JSM-6360). The different bonding information of the CNF thin films were analyzed by Fourier transform infrared spectrophotometer (IR Affinity-1S, Shimadzu, Japan). Photoluminescence spectra have been recorded by a fluorimeter (FL 4500, Hitachi).

## III. RESULTS AND DISCUSSION

### A. X-Ray Diffraction analysis for CNF thin films

Fig. 1 shows the crystalline structure of the deposited CNF thin films on Si substrates. The diffraction peaks of CNFs due to different planes such as (002), (100), (004) and (110) observed in the XRD spectrum. From the XRD peaks the interplanar spacing (3.40 Å, 2.12 Å, 1.71 Å and 1.23 Å) obtained which are well matched with the previous reported data [17]. The diffraction peak of CNFs due to 100 and 110 planes observed at 42.62 $^{o}$ and 77.45 $^{o}$ respectively. The inter-planar spacing of CNF ($d_{100}$ = 2.12 Å and $d_{110}$ =1.23) and that of graphite ($d_{100}$ = 2.13 Å and $d_{110}$ = 1.23) is shown in table -I. It observed that the inter-planar spacing of CNF and that of graphite almost same which indicates the CNFs and graphite have similar structures [18]. The details inter-planar spacing (d) values comparism is given in table III.

**Table- III: X-ray diffraction data of CNFs**

| d (XRD) | d Standard (CNF) | d (graphite) | hkl |
|---|---|---|---|
| 3.40 | 3.42 | 3.35 | 002 |
| 2.12 | 2.13 | 2.13 | 100 |
| 1.71 | 1.72 | ---- | 004 |
| 1.23 | 1.23 | 1.23 | 110 |

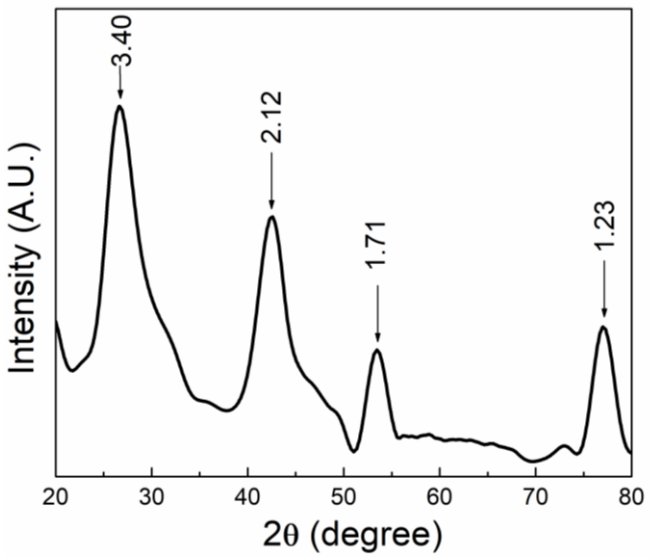



**Fig. 1. X-ray diffraction pattern of the CNF thin film deposited at 600 $^{o}$C.**

### B. Morphology analysis

The topographical image of Ni catalyst thin film for CNF preparation is shown in Fig. 2. The Ni catalyst uniformly deposited on Si substate.

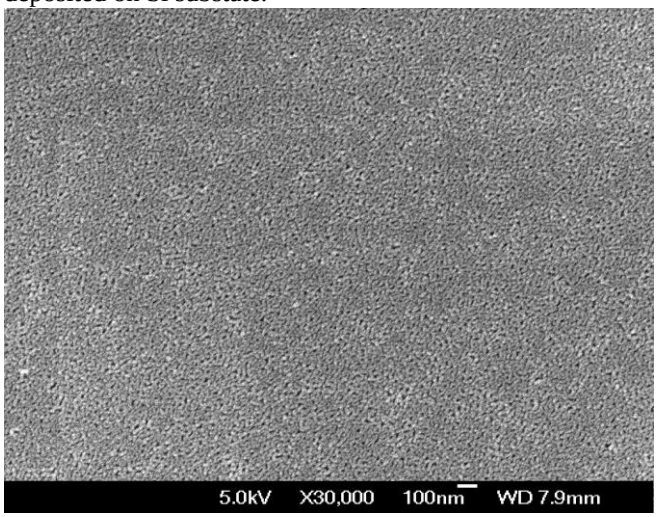
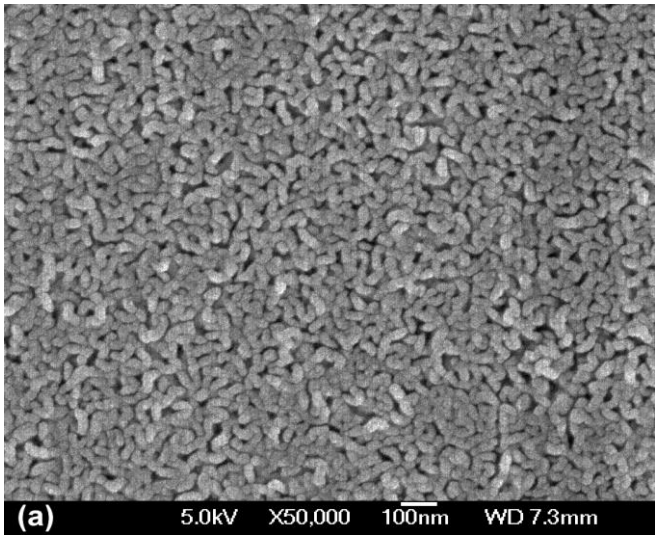



**Fig. 2. FESEM image of Ni catalyst thin film.**

Fig. 3 showed the FESEM micrographs of the deposited films, which showed the existence of carbon fibers in the films. The morphologies of the films have been changed with the change of substrate temperature.

At 500 $^{o}$C substrate temperature, only particles have been found but at 550 $^{o}$C, some carbon nanofibers have also been grown. At 600 $^{o}$C substrate temperature, carbon fibers have been grown with length ~ few μm and the corresponding diameter 300-400 nm. It is clear from these studies of substrate temperature variations that at a lower substrate temperature only particles are grown and at higher substrate temperature the morphology changes from particles to nanofibers or fibers like structure i.e. quasi one-dimensional growth takes place at higher substrate temperature.



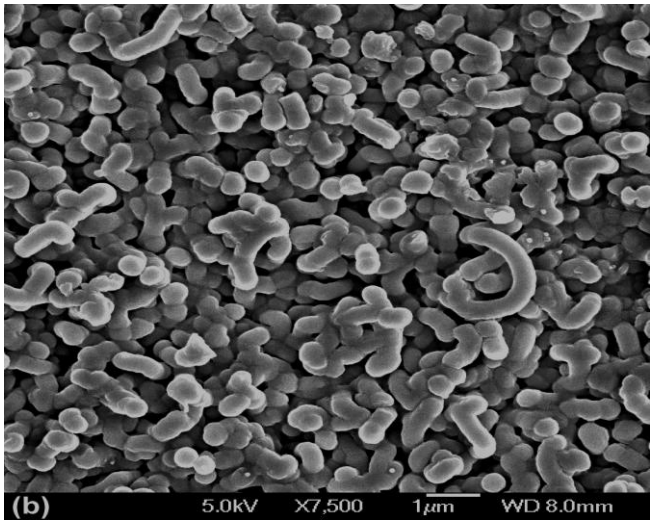




**Fig. 3. FESEM image for different substrate temperature (a) 500 °C and (b) 600 °C.**

### C. Fourier transform infrared spectroscopy Studies

Fourier transform infrared spectroscopy (FTIR) studies were carried out to analyze the bonding state of the deposited sample. The FTIR absorbance spectra of a typical film deposited on Si substrates are as shown in Fig. 4. The spectra were recorded in a FTIR spectrometer (FT-IR, SHIMADZU-8400-S) from 400 to 4000 $cm^{-1}$ by taking Si as reference and subtracting the absorption due to the Si substrate. The spectra showed different vibrational modes of various bandings. The peaks in the range of 2320 - 2365 $cm^{-1}$ are assigned due to O-C-O bond vibration of carbon di-oxide [19], from atmosphere. The peak at 1110 $cm^{-1}$ corresponds to C-C-C asymmetric stretching and C-C-O ring stretching vibration [19]. It was also observed that the very small peaks in the range of 1635-1660 $cm^{-1}$ which were assigned to be H bonded C=O weak stretching and there was a medium intense peak at 877 $cm^{-1}$ due to C-C-C symmetric stretching bond only for the sample deposited at 600 °C. This peak at 877 $cm^{-1}$ appeared only for samples deposited at 600 °C [20]. The vibrational band assignments have been shown in Table-IV.

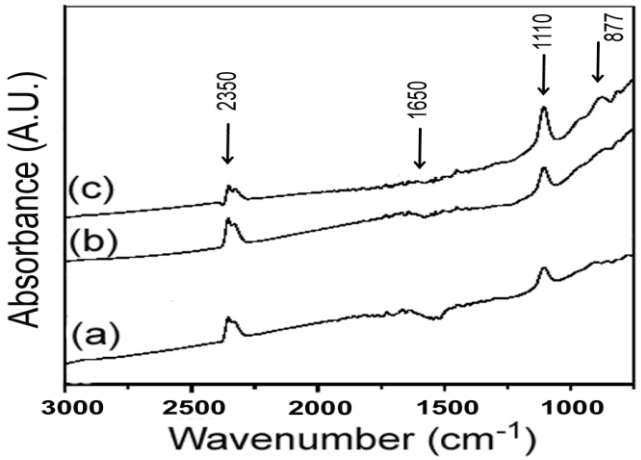



**Fig. 4. FTIR absorbance spectra of the CNF films deposited on Si substrate for different substrate temperature (a) 500 °C, (b) 550 °C and (c) 600 °C**

**Table- I: Assignment of peaks in the FTIR spectrum of CNFs**

| Vibrational peak ($cm^{-1}$) | Assignment |
|---|---|
| 2320-2365 | O-C-O bond vibration |
| 1635-1660 | H- bonded C=O stretching. (weak) |
| 1110 | C-C-O ring stretching, C-C-C asymmetric stretching |
| 850-900 | C-C-C symmetric stretching (medium) |

### D. Photoluminescence studies

Semiconducting nanotubes/nanofibers have a direct band gap in momentum space with a diameter/chirality dependent energy [21]. In a direct band gap semiconductor, where no momentum transfer is necessary for an interband transition, the likelihood of light emission from electron-hole recombination is high. A photoluminescence (PL) spectrum of carbon nanofibers is shown in Fig 5 at room temperature in air for different excitation wavelength. All the emission spectra showed a broad strong peak at 468 nm. The emission PL spectra confirms that the peak at 468 nm originates from the carbon fibers. Earlier Guo et al. [22] reported the observation of photoluminescence peak at 2.6 eV (~ 475 nm) from single walled carbon nanotubes in zeolite templates.

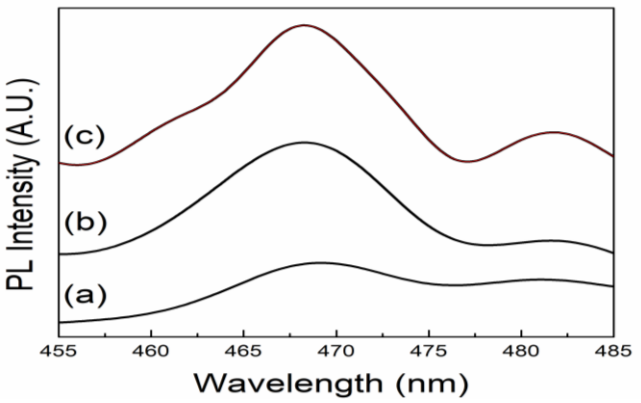



**Fig. 5. Photoluminescence spectra of the CNFs thin film deposited on Si substrate at 600 °C for different excitation (a) 300nm; (b) 350 nm and (c) 375 nm.**

## IV. CONCLUSION

Carbon nanofibers in thin film form have been synthesized on Si substrates via RF-PECVD using Ni as a catalyst. The deposition temperature has been varied from 500 - 600 $^0$C. X-ray diffraction patterns have confirmed the graphitic phase of carbon fibers. Surface morphologies of the films have been studied by using FESEM. The diameter of the carbon fibers lies in the range 300-400 nm with length in the range few μm. Fourier transformed infrared spectroscopy measurements showed different vibrational modes of carbon fibers. The morphology of the films has been changed with the change of substrate temperature and good quality fibrous films have been obtained at 600 $^o$C. A photoluminescence peak at 468 nm was observed from the carbon fibrous films. So direct band gap semiconducting carbon nanofibrous films have a promising future in opto-electronics also, among other applications.

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## REFERENCES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R.F. Curl, R. E. Smalley, "C60: Buckminsterfullerene" Nature, 354 (1985) 162-163
2. S Ijima, "Helical microtubules of graphitic carbon", Nature, 354 (1991) 56-58.
3. A. G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, R. E. Smalley, "Unraveling Nanotubes: Field Emission from an Atomic Wire", Science, 269 (1995) 1550-1553.
4. S. Tatsuura, M. Furuki, Y. Sato, I. Iwasa, M. Tian, H. Mitsu, "Semiconductor Carbon Nanotubes as Ultrafast Switching Materials for Optical Telecommunications", Adv. Mater., 15 (2003) 534-537.
5. K. Liu, Ph Avouris, R. Martel, W.K. Hsu, "Electrical transport in doped multiwalled carbon nanotubes", Phys. Rev. B, 63 (2001) 161404 (R).
6. V. V. Simonyan, J. K. Johnson, "Hydrogen storage in carbon nanotubes and graphitic nanofibers", J. Alloys and Comp., 330-332 (2002) 659-665.
7. Y. Y. Wei, G. Eres, "Directed assembly of carbon nanotube electronic circuits," Appl. Phys. Lett., 76 (2000) 3759.
8. N. Choi, T. Uchihashi, H. Nishijima, T. Ishida, W. Mizutani, S. Akita, Y. Nakayama, M. Ishikawa, H. Tokumoto, "Atomic Force Microscopy of Single-Walled Carbon Nanotubes Using Carbon Nanotube Tip", Jpn. J. Appl. Phys., 39 Part1 (2000) 3707.
9. N. Gupta, S. M. Gupta, S. K. Sharma, "Carbon nanotubes: synthesis, properties and engineering applications", Carbon Letters, 29 (2019) 419-447.
10. Y. Ando, X. Zhao, "Synthesis of Carbon Nanotubes by Arc Discharge method, New Diamond and frontier carbon technology", New Diamond and Frontier Carbon Technology, 16 (2006) 123-137.
11. C. M. Chena, Y. M. Dai, J. G. Huan, J. M. Jehng, "Intermetallic catalyst for carbon nanotubes (CNTs) growth by thermal chemical vapor deposition method", Carbon, 44 (2006) 1808-1820.
12. Y. Matsumoto, M. T. Oe, M. Nakao, K. Kamimura, Y. Onuma, H. Matsushima, "Preparation of carbon nanofibers by hot filament-assisted sputtering", Mater. Science and Eng. B, 74 (2000) 218-221.
13. S. Hondaa, K. Y. Leea , K. Fujimotoa , K. Tsujia , S. Ohkuraa , M. Katayamaa , T. Hiraob , K. Ouraa, "Formation of carbon nanofiber films by RF magnetron sputtering method", Physica B, 323 (2002) 347-349.
14. T. Ikunoa, J. T. Ryub, T. Oyamaa, S. Ohkuraa, Y. G. Baeka, S. Hondaa, M. Katayamaa, T. Hiraoc, K. Ouraa, "Characterization of low temperature growth carbon nanofibers synthesized by using plasma enhanced chemical vapor deposition", Vacuum, 66 (2002) 341-345.
15. Sk. F. Ahmed, M. Khan, N. Mukherjee, "Enhancement of Electrical Property of Carbon Nanotube by Silicon Incorporation" International Journal of Engineering and Advanced Technology, 10 (2020) 62-65.
16. T. Yanase, T. Miura, T. Shiratori, M. Weng, T. Nagahama, T. Shimada, "Synthesis of Carbon Nanotubes by Plasma-Enhanced Chemical Vapor Deposition Using $Fe_{1-x}Mn_xO$ Nanoparticles as Catalysts: How Does the Catalytic Activity of Graphitization Affect the Yields and Morphology", Journal of Carbon Research, 5 (2019) 46.
17. R. Seshadri, A. Govindaraj, N. H. Aiyer, R. Sen, G. N. Subbanna, A. R. Raju and C. N. R. Rao "Investigations of Carbon Nanotubes", Current Science, 66 (1994) 839-847.
18. JCPDS data file no. 00-013-0148.
19. C. Balazsi, Z. Konya, F. Weber, L. P. Biro, P. Arato, "Preparation and characterization of carbon nanotube reinforced silicon nitride composites" Materials Science and Engineering C, 23 (2003) 1133-1167.
20. J. Jang, J. Bae, S. H. Yoon, "A study on the effect of surface treatment of carbon nanotubes for liquid crystalline epoxide–carbon nanotube composites" J. Mater. Chem. 13 (2003) 676-681.
21. C. Deeney, S. Wang, S. A. Belhout, A. Gowen, B. J. Rodriguez, G. Redmond, S. J. Quinn, "Templated microwave synthesis of luminescent carbon nanofibers" RSC Adv., 8 (2018) 12907-12917.
22. C. Li, G Shi, "Carbon nanotube-based fluorescence sensors" J. of Photochemistry and Photobiology C: Photochemistry Reviews, 19 (2014) 20-34.

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