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Effect of tungsten/filament on the growth of carbon nanotubes in hot filament chemical vapor deposition system

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Multi-wall Carbon nanotubes are successfully grown on Si (100) substrate in the hot filament chemical vapor deposition system without using the external catalyst. High resolution scanning electron microscopic images of the deposited films show a long noodle shape and vertically grown carbon nanotubes distributed uniformly over a large area of the substrate with relative high growth density. HRTEM studies show that the grown tubes are multi-walled. The diameter of the nanotubes is about 20 nm and the thickness of the grown film is $\sim$1.2 μm. From XRD and EDAX analyses traces of catalyst materials (Fe, Co, Ni etc.) are not found except tungsten, which might be on the surface of the film. X-ray photoelectron spectroscopy (XPS) indicates that presence of Carbon (C_{1s}). Micro Raman spectroscopy and HRTEM study reveal that the grown tubes are multi-wall which are partially crystallized.

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1. Introduction

In the recent years, novel carbon materials such as diamond thin films, diamond like carbon coatings, fullerene and carbon nanotubes have been intensively investigated because of their great potential applications. A variety of techniques have been developed for the synthesis of these novel carbon materials, among them chemical vapor deposition (CVD) technique has been proven to be a very versatile tool. This technique is being used to synthesize highly oriented diamond thin films, fullerene, decorated and branched carbon nanotubes in the past [1–8]. The deposition of such complex structures has come up with several surprises including the carbon nano-onions [5], single and multi-walled carbon nanotubes [1–16], nano-horns [7] and carbon micro-trees [8, 9]. The unique atomic structures have exhibited interesting electronic and mechanical properties arising from the reduced dimensionality. Beside the academic interest in nanoparticles, recent research is aimed towards the industrial applications such as use in cold-field electron emitters for 2-D display devices, X-ray generation and hydrogen storage materials [10–12].

The final shape is mainly determined by two driving forces being; (i) preferential growth of the graphene lattice planes and (ii) the tendency of graphene plane to bend. The non-thermal equilibrium conditions necessary for growth of carbon nanoparticles are usually established by arc discharge [13], laser ablation [14], pyrolysis and catalytic methods [13–16]. Recently the use of plasma enhanced CVD and thermal CVD methods for synthesizing the nanoparticles are reported too [4, 9, 12, 16]. Growth of carbon nanotubes on catalyzed Si substrate in HFCVD system is also reported [17–21]. Various reports are available for the growth of single as well as multi-walled carbon nanotubes using HFCVD system but all the works are carried out using a single or multiple catalyst (Ni, Co, Fe, graphite fiber etc.) but as such no reports available for the in-process catalyst [22–26]. In the present work a in-process catalyst (from the tungsten filament) is found to activate CNT growth. As such, to our knowledge, reports are not available for the use of W as catalyst. Although massive production of carbon nanotubes has been realized by arc discharge and laser ablation, controlling diameters, length and preferable alignment of carbon nanotubes has never been easily possible with such approaches. Moreover, fabrication of carbon nanotubes on plain Si substrate is of technological importance for the application to future Si based opto-electronic devices.

In this paper we present the synthesis of carbon nanotubes (wounded/noodle like shaped) on a plain silicon surface, without the use of a nucleation agent or external catalyst, grown by hot tungsten filament chemical vapor deposition system with a gaseous mixture of CH_4 and H_2. In the present work, it is found that the tungsten from the hot filament work as catalyst. The results are discussed using the structural analysis carried out using

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SEM, FESEM, HRTEM, GAXRD, XPS and Raman spectroscopies etc. and are correlated to the deposition conditions.

2. Experimentation

Carbon nano-wires/tubes were deposited using HFCVD system as reported earlier for the growth of diamond film [27]. A *p*-type Si (1 0 0) wafers of size 15 × 7 × 0.5 mm^3 were used as substrates. The substrates were degreased in boiling acetone, tri-chloro-ethylene and methanol (all AR grade) and then loaded onto a substrate holder. The assembly was then transferred to the high-vacuum reaction chamber. Substrate is aligned horizontally at the center of the chamber just above the tungsten filament (length 15.0 and 5.0 mm cross sectional diameter), perpendicular to the gas flow direction. Distance between the substrate and filament was adjusted to ∼4 mm by using the manipulator.

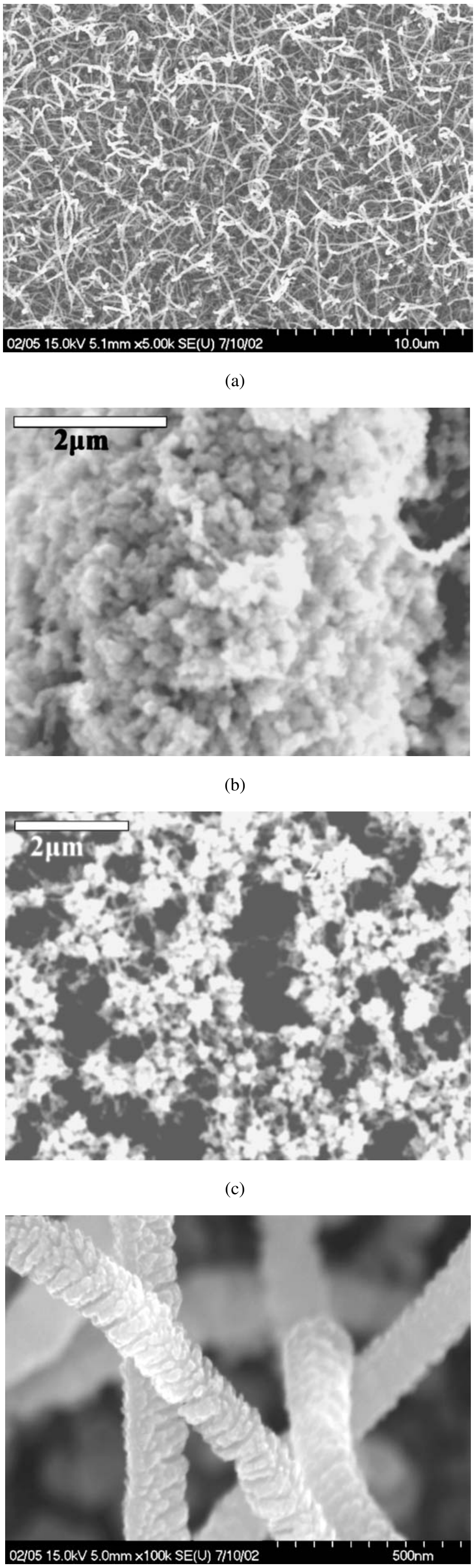
A mixture of high purity H_2 (99.999%) and CH_4 (99.95%) gases (ratio 100:1) was introduced from the bottom side of the chamber and the flow rates were controlled using mass flow controllers (MFC). A total flow rate of 100 sccm was passed and the total gas pressure inside the reaction chamber was kept constant as 4 ± 0.25 kPa, throughout the deposition process. Deposition was carried out at the substrate temperature of 900, 925 and 950°C (referred hereafter as sample a, b and c respectively). The substrate temperature was measured by thermocouple and the filament temperature, kept as 2400 ± 50°C, was measured by optical pyrometer (Minolta TR-630, Japan). Deposition was carried out for two hours. In this experiment, substrates were not flashed (by heating up to 1200°C in vacuum) like previous reported work of our group for the growth of diamond [27].

Surface morphological study of the deposited films was carried out using SEM (JSM-6400, Jeol), FE-SEM (S-4700, Hitachi) and the structural analyses was carried out with glancing angle XRD (Rigaku), XPS (ESCALB 250, source: Mg K_α) and Micro Raman spectroscopy (Renishaw micro Raman 2000, He-Ne laser, $\lambda = 632.8$ nm).

3. Results and discussion

The XPS spectrum of the silicon substrate taken after degreasing and before deposition shows the peaks corresponding to Si_{2p}, Si_{2s}, C_{1s} and O_{1s} as observed in our earlier experiments [22]. It was realized that after flashing, O_{1s} and C_{1s} peaks disappear.

Fig. 1a–c shows top view SEM images of the deposited film on samples a, b and c respectively. It can be seen in Fig. 1a that the tubes are grown uniformly over the entire Si substrate with a relatively high growth density. Whereas in Fig. 1b and c, carbonaceous particles (amorphous carbon) can be seen. These are seen to be having long noodle shape structure and appear like wounded nanotubes. Fig. 1d show FESEM image of the tubes. Fig. 1e present the cross sectional SEM image of the sample a, which shows that the tubes are



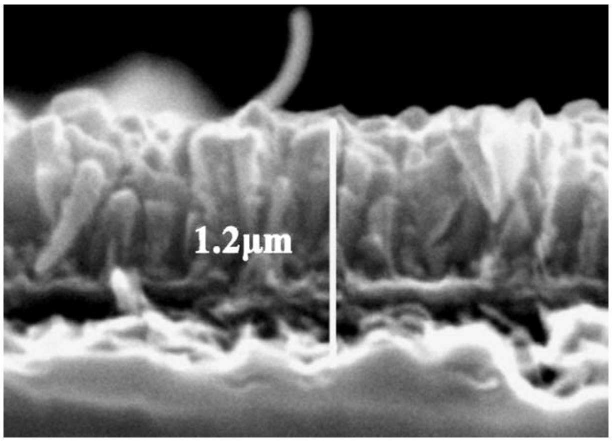
(a)

(b)

(c)

(d)

Figure 1 (a–c) Top view SEM images of the films deposited at (a) 950°C (b) 925°C and (c) 900°C for two hours. (d) FESEM image of the film deposited at 950°C. (e) Cross sectional SEM image of the film deposited at 950°C. (*Continued*)



(e)

Figure 1 (*Continued*).

grown vertically and the thickness of the film (height of the tubes) is about 1.2 μm.

A HRTEM image of the sample 'a' is shown in Fig. 2. The inset in Fig. 2 is the magnified image of the box marked area. It can be clearly seen that the tubes are multi-wall with tube diameter of about 20 nm.

Fig. 3a shows a wide scan XPS of sample a. It shows peaks corresponding to various shells of tungsten, argon, carbon, oxygen and copper. It is worth nothing that peaks corresponding to Co, Fe, Ni and other metals except tungsten, which could have evaporated from HFCVD chamber, are not seen. This indicates that the growth in the present case is not due to the above materials, which are reported to act as catalyst but at the same time traces of tungsten are seen which are likely to be on the surface of the film. The possibility of tungsten working as catalyst in the growth of nanotubes can not be ignored. The appearance of $Cu_{2p1/2}$ is due to the substrate holder since for XPS study, substrate was mounted on Cu holder and tungsten evaporated from the hot filament.

In HFCVD process, the tungsten filament is subjected to a hydrogen/methane atmosphere at temperature ranging from 1800 to 2500°C and pressure from 0.1 to 15 kPa. Depending on the process parameters, the filament undergoes structural changes and tungsten monocarbide (WC), tungsten dicarbide (W_2C) or solid graphite phases can form. Since the hydrogen dissociation, which takes place on the surface of the filament, and the heating of substrate and gas phase by radiation from the filament, play crucial roles during diamond or CNT deposition, the exact condition of the filament must be known and controlled. Zeiler [28] have studied the structural changes in the filament during HFCVD process. It is reported that the a time dependent phase transformation of tungsten filament occurs. During the

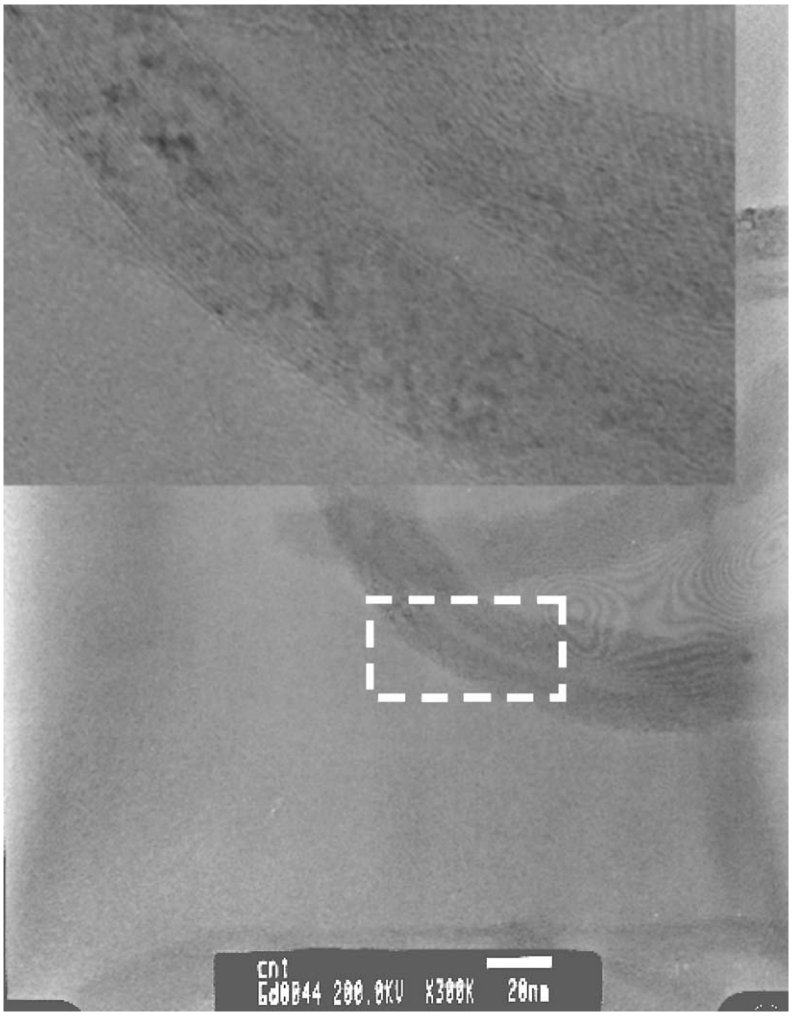


Figure 2 HRTEM image of the sample deposited at 950°C. Inset is the magnified image of the box marked area.

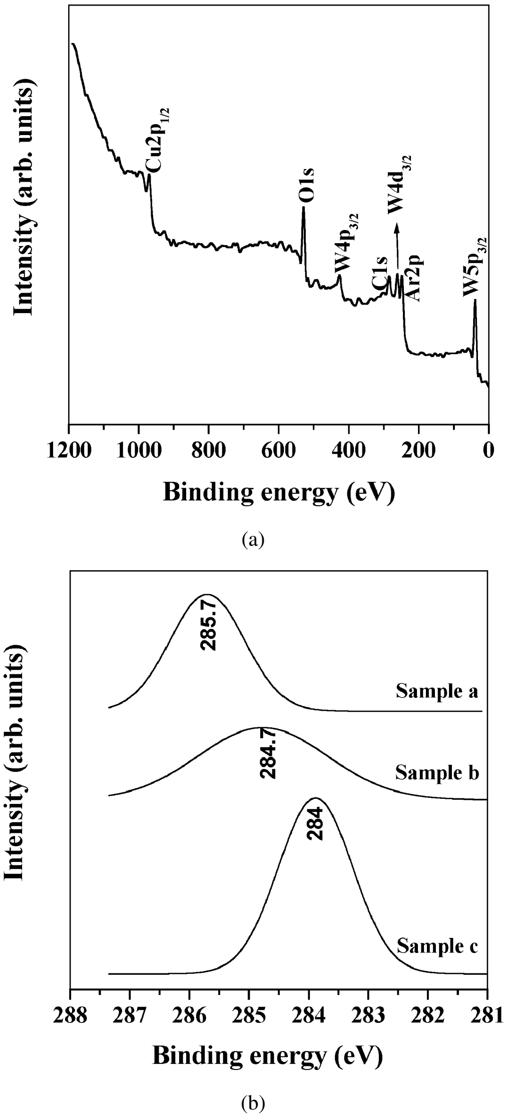


Figure 3 (a) Wide scan XPS spectrum of the films deposited at (a) 950°C (sample a) for two hours. (b) Core level C_{1s} XPS spectra of the films deposited at (a) 950°C (sample a) (b) 925°C (sample b) and (c) 900°C (sample c) for two hours.

first hour of hot filament CVD, distinct changes in the gas phase occur and the filament temperature decreases when heated in methane/hydrogen atmosphere. The first step of the phase transformation is the formation of W_2C. Methane dissociation on the filament surface was found, to be the rate determining step of this process. As soon as the W_2C formation is complete, different WC growth kinetic starts. This indicates that initially the filament is carburized, by dissociation of CH_4, forming carbide phase and this in turn help in the initial nucleation of the diamond/CNT in HFCVD process as the substrate and filament gas is very low (~4 mm).

The core level (C_{1s}) XPS spectra of the carbon nanotubes, grown on samples a, b and c, are presented in Fig. 3b respectively. In all three samples, C_{1s} peak is appeared at 285.7, 284.7 and 284 eV, which clearly confirms that the film composition is basically carbon.

An attempt is made to fit the core level C_{1s} XPS curves for all three samples using Shirley-type base line with mixed Gaussian (30%) and Lorentzian (70%) profile and controlled FWHM. The entire curve fitting was carried out with chi-squared value less than 2 eV, which is reported to be good value for best fitting [29]. The corresponding spectra are shown in Fig. 4a–c respectively. It can bee from Fig. 4a, that it consist of two peaks at 286 and 285.5 eV, whereas Fig. 4b and c shows that the C_{1s} spectra consist of many peaks relating to amorphous carbon [29]. This indicates that the grown films are not fully crystallized and contain amorphous carbon.

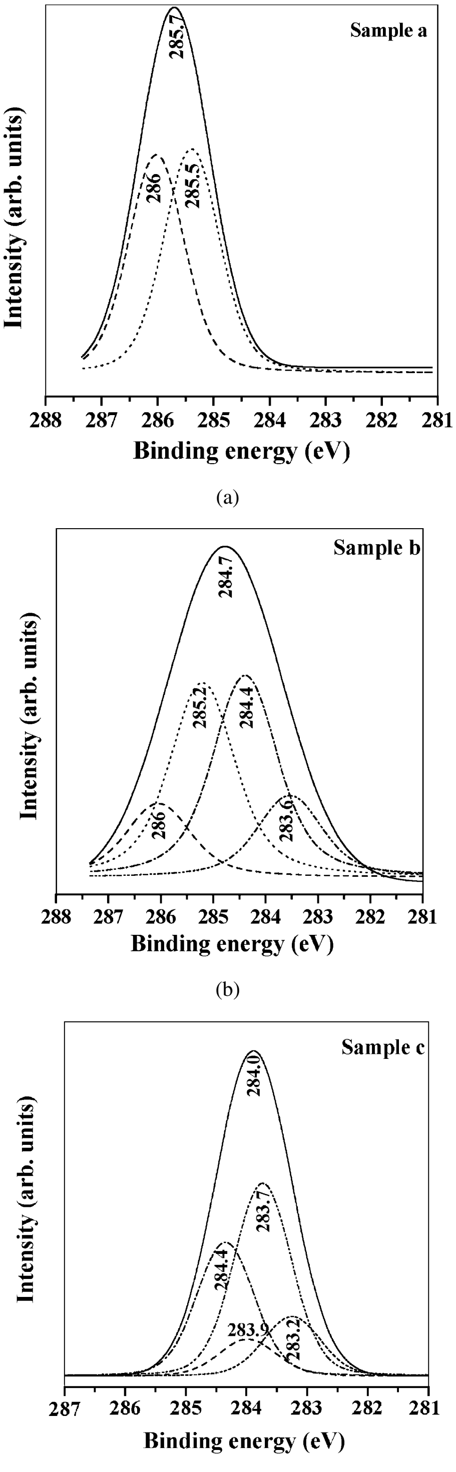


Figure 4 (a–c) Curve fitting for the C_{1s} XPS spectra of the films deposited at (a) 950°C (b) 925°C and (c) 900°C.

An elemental analysis of all the three samples was carried out using glancing angle XRD (GAXRD) with an X-ray (Cu K_{α}) incidence angle of 0.5° and Bragg angle ranging from 20 to 110°. The corresponding

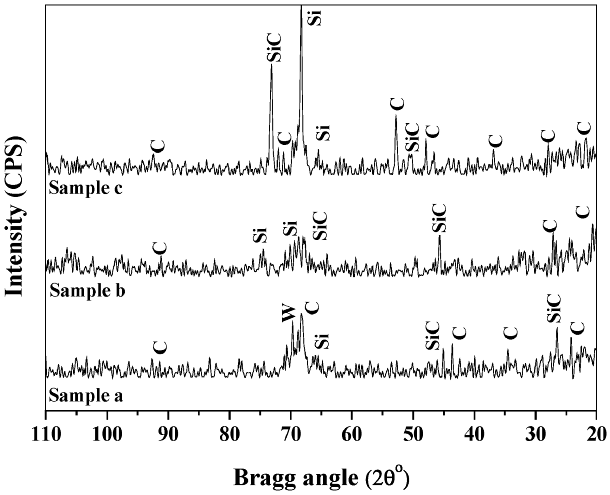
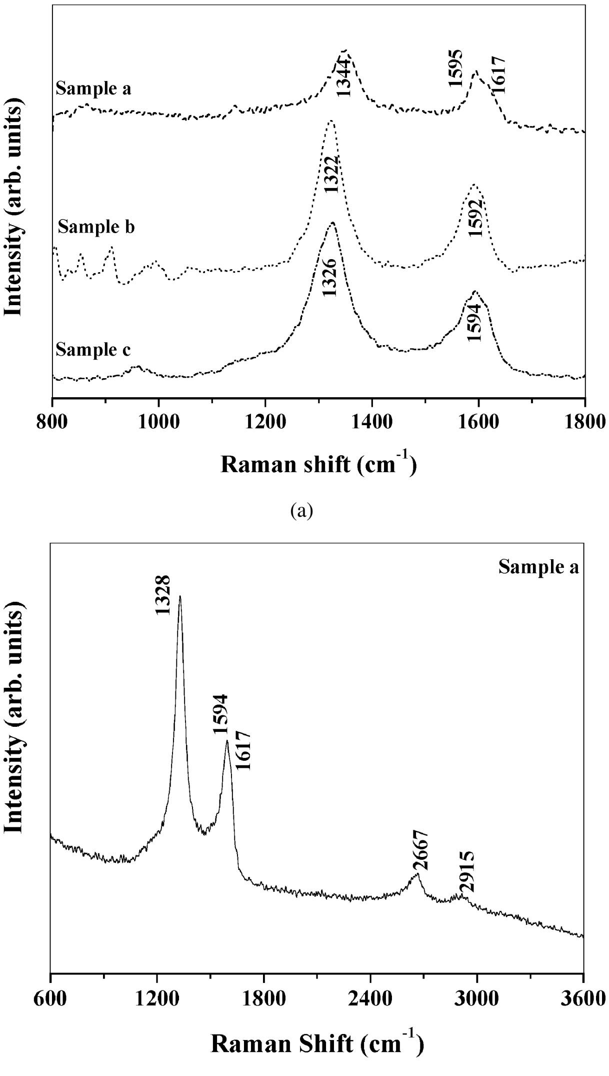


Figure 5 Glancing angle XRD of the films deposited at (a) 950°C, (b) 925°C and (c) 900°C with an X-ray incident angle of 0.5°.

spectra are shown in Fig. 5. It can be seen that it consist of carbon as major phase and few peaks of SiC, Si and W are seen (JCPDS cards, 46-09443-45, 47-0787,47-1154, 42-1360, 39-1196, 41-1111,47-1187, 47-1319). The traces of Fe, Ni, Co and other metals are also not found in these spectra. EDAX analysis of sample ‘a’ showed the presence of 10.5% Oxygen, 35.9% Si, 9.2% Ca and 0.8% tungsten. It can be seen that the tungsten percentage is quite small. The appearance of W is due to the evaporation from the hot filament as filament temperature is very high and gap between substrate and filament is very less (∼4.0 mm).

First order Raman spectra of the film grown on three different samples are presented in Fig. 6a. In all the samples, two peaks are clearly seen located at 1322–1344 cm^{-1} and 1592–1595 cm^{-1} respectively. The peak at ∼1595 cm^{-1} (G-line) corresponds to the high frequency E_{2g} mode, which originates due to the movement in the opposite direction of two neighboring carbon atoms in a graphite sheet. In case of sample a, shoulder is also seen at 1617 cm^{-1}. Wenzhi [30] reported that nanotubes produced using hydrocarbon gases show an additional strong band at ∼1348 cm^{-1} (D-line) and a weak band around 1617 cm^{-1} (D′ line). A similar phenomenon is observed in the present study. This peak is reported to be similar to that of PG, which may not be observed in the spectra of HOPG [30]. The origin of D and D′-lines in other form of carbon materials has been reported as disordered features due to finite particle size effect or lattice distortion. In other words, the relative intensity of D-line with respect to G-line mode depends on the crystal planar domain size of graphite [30].

A wide scan Raman spectrum of sample a, is shown in Fig. 6b, which shows four peaks at 1328, 1594, 2667 and 2915 cm^{-1}. The peak at 2667 cm^{-1} is a second order D-line peak whereas the weak broad peak at 2915 cm^{-1} is just a combination of D and G lines. It is noticed that the peak corresponding to the breathing mode of nanotubes vibrating along the radial direction is absent. From this spectrum, it can be concluded that the grown tubes are ‘multi-wall nanotubes.’ The Raman spectra obtained in the present case is similar to that of reported spectra of multiwall carbon nanotubes [16, 31–34]. The intensity G line being lower than that of the D-line indicates a bad crystallization of the nanotubes. This supports the results obtained after the core level XPS curve fitting (Fig. 4a), which shows ∼40% amorphous and ∼60% crystalline.



(a)

(b)

Figure 6 (a) First order Raman spectra of the films deposited at (a) 950°C, (b) 925°C and (c) 900°C for two hours. (b) Wide scan Raman spectra of the films deposited at 950°C for 2 h.

The appearance of peaks corresponding to D-line, which may be originating from defective carbon or carbonaceous particles (1322–1358 cm^{-1}), can also be due to following reason. It is reported that diamond and carbon nanotubes, both being allotropes of carbon, have some structural resemblances with sp^3 chemical bond. Under the conditions of HFCVD, especially in the presence of H_2 and due to high substrate temperature, the sp^2 bonds of the tubes can open and turn into sp^2 dangling bonds, and finally turns into sp^3 bonds [31–34]. This process results in a countless heterogeneous nucleation sites causing the improvement of nucleation and growth of carbon structures, resulting in a higher density.

The appearance of carbonaceous particles (amorphous carbon), as evidenced from the SEM studies and Raman spectroscopy, can be correlated to the low deposition temperature. It is reported by Kurt [9] that increase in substrate temperature changes the structure of carbon from a disordered needle like structure via a network of worm-like structure to a larger and straighter wire like structure. A similar phenomenon was observed in the present study as deposition was carried out at the substrate temperature of 900 to 950°C from sample to sample and the changes in the morphology of the deposited film are seen in SEM images (Fig. 1). Still further studies are required to optimize the deposition temperature.

In the present study, carbon nanotubes were grown on plain Si substrate without using any external catalyst. Though CNT of various shapes and structures can be grown easily with the use of different techniques and catalysts, but the control of nucleation, growth and uniformity still desire further investigations. It is not yet clear how the nano-structures can grow on surface of pure Si substrate (catalyst free surface) autocatalytically. As it is known, that during the deposition of diamond or carbon nanotubes in HF-CVD system, the SiC and WC grows initially as a nucleation cursor and then plays an important role for the growth of carbon based structures [9, 20–22]. Therefore, these may be acting as a catalyst for the nanotubes also. It is reported that W can be used as catalyst for the growth of carbon nanotubes but suppresses the formation of tube and at the same time increases the yield of encapsulated Co particles [20, 21]. The general nanotubes growth mechanism using a catalyst in a CVD process involves the dissociation of hydrocarbon molecules catalyzed by transition metal, and dissolution and saturation of carbon atoms in metal nanoparticle. The precipitation of carbon from the saturated metal particle leads to the formation of tubular carbon solids in a sp^2 structure, Tubular formation favored over other forms of carbon such as graphitic sheets with open edges, which is due to the fact that tubes does not contain dangling bonds and therefore are in low energy form [1].

4. Conclusion

In the present work, multiwall carbon nanotubes are grown on Si surface using hot filament CVD. The grown CNT are distributed uniformly over the Si surface in a long noodle shape structure (wounded tubes) with relatively high growth density. The diameter of the tubes estimated to be ∼20 nm (from HRTEM images) and thickness of the film is about 1.2 μm. GAXRD and EDAX, XPS studies indicated that even though external catalyst are not used for the growth but tungsten seems to worked as catalyst for deposition. Raman spectrum and HRTEM studies reveals that the deposited CNT are multiwall carbon nanotubes, which are partially crystallized. Elemental analysis by XPS indicates the presence of C_{1s} phase. The quality of the carbon nanotubes can still be improved by purification.

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References

1. HONGJIE DAI, *Surf. Sci.* **500** (2000) 218.
2. M. S. DRESSELHAUS, G. DRESSELHAUS and PH. AVOURIS (eds.), Carbon Nanotubes-Synthesis, Structure, Properties and Applications (Springer, Germany, 2001) p. 30.
3. T. TANAKA, T. YAMABE and K. FUKUI, (Eds.), “The Science and Technology of Carbon Nanotubes” (Elsevier, UK, 1999) p. 29, 51.
4. L. CHOW, D. ZHOU, A. HUSSAIN, S. KLECKLY, K. ZOLLINGER, A. SCULTE and H. WANG, *Thin solid Films* **368** (2000) 193.
5. D. UGARTE, *Nature* **359** (1992) 707.
6. S. IJIMA, *ibid.* **354** (1991) 56.
7. S. IJIMA, M. YUDASAKA, R. YAMADA, S. BANDOW, K. SEUNAGA, F. KOKAI and K. TAKAHASHI, *Chem. Phys. Lett.* **309** (1999) 165.
8. P. M. AJAYAN, NUGENT, R. W. SIEGEL, B. WEI and PH. KOHLER-REDLICH, *Nature* **404** (2000) 243.
9. RALPH KURT, AYATOLLAH KARIMI and VOLKER HOFFMANN, *Chem. Phys. Lett.* **335** (2001) 545.
10. J. M. BONARD, J. P. SALVETAT, T. STÖCKLI, L. FORRÓ, K. KERN and A. CHÂTELAIN, *Appl. Phys.* A **69** (1999) 245.
11. Y. SAITO, K. HAMAGUCH, K. HATA, K.T. KASUYA, A. KASUYA and Y. NISHINA, *Ultramicroscopy* **73** (1998), 1.
12. Z. F. REN, Z. P. HUANG, D. Z. WANG, J. G. WEN, J. W. XU, J. H. WANG, L. E. CALVET, J. CHEN, J. F. KLEMIC and M. A. REED, *Appl. Phys. Lett.* **75** (1999) 1086.
13. S. IJIMA and T. ICHIHASHI, *Nature* **363** (1993) 603.
14. D. S. BETHUNE, C. H. KIANG, M. S. DE-VRIES, G. GORMAN, R. SABPU, K. VAZQIES and R. BAYERS, *ibid.* **363** (1993) 605.
15. A. THESS, R. LEE, P. NIKOLAEV, H. DAI, P. PETIT, J. ROBERT, C. XU, Y. H. LEE, S. G. KIM, A. G. RINZLER, D. T. COLBERT, G. E. SCUSERIA, D. TOMÁNEK, J. E. FISCHER and R. E. SMALLEY, *Science* **273** (1996) 483.
16. C. J. LEE, D. W. KIM, T. J. LEE, Y. C. CHOI, Y. S. PARK, W. S. KIM, Y. H. LEE, W. B. CHOI, N. S. LEE, J. M. KIM, Y. G. CHOI and S. C. YU, *Appl. Phys. Lett.* **75**(12) (1999) 1721.
17. BO GAN, J. AHN, QING ZHANG, S. F. YOON, RUSLI, Q.-F. HUANG, H. YANG, M. B. YU and W. Z. LI, *Diamond Relat. Mater.* **9** (2000) 897.
18. A. M. BONNOT, M. DELDEM, E. BEAUGNON, T. FOURNIER, M. C. SHOULER and M. MERMOUX, *ibid.* **8** (1999) 631–635.
19. A. M. BONNOT, M. N. SEMERIA, J. F. BORONAT, T. FOURNIER and L. PONTONNIER, *ibid.* **9** (2000) 852.
20. C. J. LEE, S. C. LYU, H. W. KIM, J. W. PARK, H. M. JUNG and J. PARK, *Chemical Phys. Lett.* **361** (2002) 469.
21. C. H. KIANG, A. G. WILLIAM, B. ROBERT, J. R. SALEM and S. B. DONALD, *J. Phys. Chem. Solids* **57**(1) (1996) 35.
22. S. G. WANG, J. H. WANG, Z. B. MA, C. X. WANG, W. D. MAN and B. H. ZHANG, *Diamond Relat. Mater*. **12** (2003) 2175.
23. SHEN ZHU, CHING-HUA SU, S. L. LEHOCZKY, I. MUNTELE and D. ILA, *ibid.* **12** (2003) 1825.
24. Y. B. ZHU, W. L. WANG, K. J. LIAO and Y. MA, *Diamond Relat. Mater.* **12** (2003) 1862.
25. CH. TÄSCHNER, F. PACAL, A. LEONHARDT, P. SPATENKA, K. BARTSCH, A. GRAFF and R. KALTOFEN, *Surf. Coat. Technol* **174–175** (2003) 81.
26. W. AHMED, H. SEIN, N. ALI, J. GRACIO and R. WOODWARDS, *Diamond Relat. Mater.* **12** (2003) 1300.
27. C. V. CHIEM, J. H. KIM, H. S. SHIN and J. M. SEO, *J. Vac. S. and Tech.* A **20**(1) (2002) 202.

28. E. ZEILER, S. SCHWARZ, S. M. ROSIWAL and R. F. SINGER, *Mater. Sci. Eng.* A **335** (2002) 236.
29. B. V. CRIST, "Handbook of Monochromatic XPS Spectra, The Elements of Native Oxides" (John Wiley & Sons Ltd., New York, 2000) p. 45.
30. LI WENZHI, HAO ZHANG, WANG CHAOYING, ZHANG YUN, XU LIWEN and ZHU KE, *Appl. Phys. Lett.* **70**(20) (1997) 2684.
31. X. ZHAO, Y. ANDO, L. C. QIN, H. KATAURA, Y. MANIWA and R. SAITO, *Physica* B **323** (2002) 265.
32. P. C. EKLUND, J. M. HOLDEN and R. A. JISHI, *Carbon* **33**(7) (1995) 959.
33. R. J. MEILUNAS, R. P. H. CHANG, S. LIU and M. M. KAPPES, *Appl. Phys. Lett.* **59**(26) (1991) 3461.
34. D. M. GRUEN, S. LIU, A. R. KRAUSS and X. PAN, *J. Appl. Phys.* **75**(3) (1994) 1758.

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