Effect of different metal catalysts on the growth of Carbon Nanotubes by chemical vapor deposition using five step process

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Carbon nanotubes are synthesized by using chemical vapor deposition method in which Iron, Nickel and Cobalt are used as catalyst. By chemical vapor deposition decomposition of acetylene is achieved at 850°C and the carbon was deposited on different substrates (Glass and Silicon) in the presence of catalyst for the carbon nanotube growth. The effect of different metal catalysts on the growth of the carbon nanotubes is studied by the experiment performed. The carbon nanotubes synthesized by different catalysts on different substrates are characterized using Scanning electron microscopy (SEM), X-ray diffraction (XRD) techniques and transmission electron microscopy (TEM). The experimental work for the synthesis of CNTs is performed at MRC, MNIT Jaipur. In this paper, the synthesis of carbon nanotubes is reported and also their fabrication and characterization. The reported procedure for the synthesis of carbon nanotubes is a five step process for CVD in order to obtain a high yield and purity.

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1. Introduction

From last few decades, nanotechnology is a growing field in research [1]. Due to their extraordinary electrical and thermal properties, carbon nanotubes (CNTs) attracted lot of attention of researchers all over the world [2-4]. Carbon nanotubes (CNTs) have very high tensile strength and Young's modulus. They can be either metallic or semiconductors depending on their geometry [5]. CNTs are generally produced by three methods as arc discharge method [7, 8], laser ablation method [9, 10] and thermal chemical vapor deposition method [11-14]. In laser ablation and arc discharge method graphite is vaporized by high intensity laser beams and electrical arcs respectively, and then vapors are allowed to condense. In chemical vapor deposition method, a thin film of transition metal-containing catalyst solution is deposited on substrate by using different thin film coating techniques such as spin coating, dip coating or sputtering [15]. Then, decomposition of carbon containing gas like acetylene, methane and other hydrocarbon is carried out in the presence of transition metal containing catalyst at a very high temperature [16].

In CVD method, CNTs can grow on the area coated with metal catalysts and they get self-assembled by the intra-tube Vander- Waals interactions [17]. Catalytic metals, such as Iron, Cobalt and Nickel are popular means of CNT growth using CVD [18]. The advantages of CVD are the possibility of large scale continuous production, low temperature and controllability [19].

In this paper, CNT growth and its characterization on silicon substrates using catalytic chemical vapor deposition method at temperature 850°C was reported. The effect of three different metal catalysts (Iron, Nickel and Cobalt) on CNT growth has been analyzed. Acetylene gas is used as carbon-containing gas. It is observed that CNT growth was more for Iron catalysts at the reported temperature of 850˚C as compared to Cobalt and Nickel catalysts. A large number of well graphitize carbon nanotubes having uniform diameters and of large size are grown in the reported CVD process when Iron is used as catalyst on Si substrate.

2. Fabrication of carbon nanotubes

2.1 Sample Preparation Procedure

A silicon wafer (p-type Si) and glass cut in dimensions 1X1 cm^2 is used as the substrate. First of all, the glass and silicon substrates are cleaned chemically in acetone for 30 min in ultrasonic bath. The catalyst solutions contains 100mM of $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ or $Co(NO_3)_2.6H_2O$ dissolved in 150mM ethanol. The catalyst solutions is stirred using magnetic stirrer at temperature 45°C for 30 minutes [15]. After that, layer of catalyst solution is deposited on as-prepared substrates. A spin coating system is utilized to deposit very thin film of few microns of three different catalysts on Glass and Si substrates. The spin coating system includes a

substrate holder which is able to rotate, a rotor and a vacuum creator. The substrate holder is rotated with a speed of 500 revolutions per minute.

2.2 Experiment Procedure

A substrate as-prepared was placed in the CVD tube (Technos instrument STF 1200 tube furnace) for synthesis. The synthesis process proceeded in five steps. In first step, the CVD tube is evacuated to 10 mTorr. After reaching low pressure of 10 mTorr, the growth temperature is set in the steps of 5°C/min. Then catalyst was annealed to 650°C (in the steps of 5°C/min) under the flow of Hydrogen and Argon gas. The flow rate of the gas was controlled by electronic mass flow meters. A constant flow of Hydrogen and Argon gas was maintained for duration of 2 hr 10 min until the temperature of CVD tube reached to 650°C as shown in figure 1. At this high temperature reduction of metal oxides into metal particles takes place under the flow of Hydrogen gas. At 650°C flow of hydrogen gas was stopped and flow of acetylene gas was allowed in the furnace tube by opening the acetylene vent of CVD. At 750°C acetylene starts to dissociate into its constituents. After reaching the temperature 750°C, the gas flow of Argon was stopped and flow of Hydrogen and Acetylene gas were continued for next 10 minutes [11, 14]. After 10 minutes, flow of Argon gas was allowed in the CVD tube and temperature is ramped to 850°C. After reaching 850°C, gas flow of Argon was stopped and flow of acetylene and Hydrogen is continued for 30 minutes. The flow of Hydrogen gas at this high temperature increase the yield of well-graphitize CNTs as it provides the more nucleation sites for the growth of CNTs [20]. At temperature 850°C the following reaction takes place:-

$$C_2H_4 + H_2 \xrightarrow{\text{Catalysts, 850°C}} 2C(s) + 3H_2(g)$$

The above reaction indicates that when acetylene reacts with Hydrogen in the presence of catalyst at 850°C temperature, the carbon gets deposited in the form of carbon granules on the substrate.

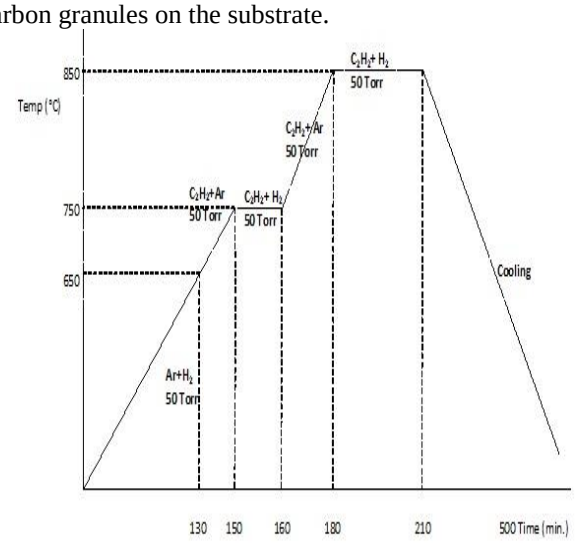

Fig. 1 Flow chart of experiment

After a predetermined time of deposition, the growth was terminated by turning off the hydrogen and acetylene gas flow. The sample is then allowed to cool for 5 hours up to room temperature and settle at that temperature. Same procedure is followed for other substrates having Cobalt and Nickel as catalyst. It is observed that when Nickel as catalyst is used, to increase the yield of CNT (as that reported) the appropriate temperature requirement is around 950˚C. The results at this temperature are not reported in this paper.

When CVD method is used for the synthesis of carbon nanotubes, Hydrogen gas is used to reduce metal oxides into metal particles. Catalyst in the form of metal oxides shows a stronger interaction with oxidized substrates which causes lower mobility [21]. Hydrogen penetrates into subsurface layers and loosens this interaction, which may give higher carbon diffusivities for CNT nucleation. Amorphous carbon increases the excitation energy required for the synthesis of CNTs. As a weak oxidizer Hydrogen helps in removing amorphous carbon and will increase the active time of catalyst particle [22]. In the earlier CVD methods, the decomposition time of hydrocarbon gas was small. In order to reduce defects and to increase the yield of CNTs a five step CVD method is used in this paper as compared to three step CVD method reported in literature.

2.3 Characterizations

The as-grown CNTs are characterized by NOVA NanoSEM 450 Scanning electron microscopy (SEM), Tecnai G^2 20 (FEI) S-Twin 200kv Transmission Electron Microscopy (TEM), Xpert Pro PANalytical X-Ray Diffraction (XRD) and EDS analysis. SEM is used to see the orientation and to focus on the composition of as-grown CNTs. In order to see what is inside or beyond the surface TEM is used. TEM characterization gives information about the structure and type of the CNTs as being single-walled CNTs and multi-walled CNTs. The X-ray diffraction technique is utilized to obtain structural information about crystalline solids and to obtain fast identification of materials. Percent CNT coverage (by) area was estimated using EDXA analysis. The effect of different metal catalysts on the CNT growth is studied in the experimental work reported in this paper. It can be seen that CNT grows more densely for iron catalysts as compared to Cobalt and Nickel as the reported temperature is 850˚C for the synthesis of CNT.

3. Results

In order to obtain structural information about crystalline solids and to get fast identification of CVD output, X-ray diffraction technique (at MRC, Jaipur) is used. The strong diffraction peak at 26.54° (i.e. at Position (*2 Theta (copper (Cu))) indicates the preferential growth of carbon nanotubes, oriented along the c-axis and confirms good crystalline nature. Other peak in the

diffraction pattern corresponds to the presence of Iron, Iron-Carbide and Iron-oxide particles.

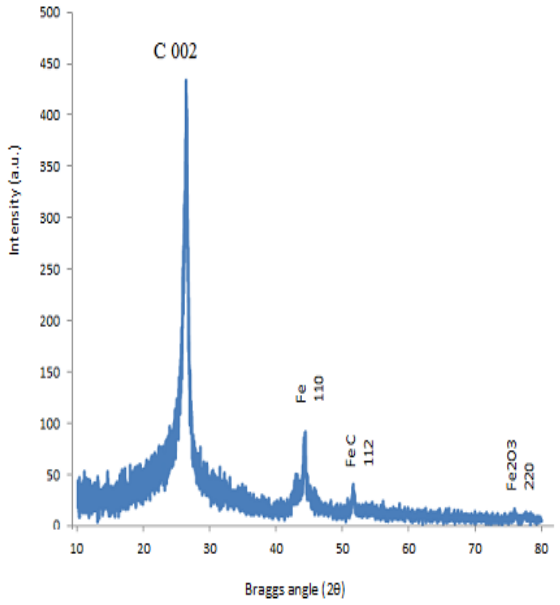

Fig 2: XRD spectra of the as-grown CNTs at 850°C by chemical vapor decomposition of acetylene

Percent CNT coverage (by) area in the sample output of CVD method was estimated using Energy Dispersive X-Ray analysis. As shown from the EDXA result in Fig. 3, sample output of CVD has mostly carbon in its contents with a very small percentage of Iron particles which was used as catalyst in the growth process.

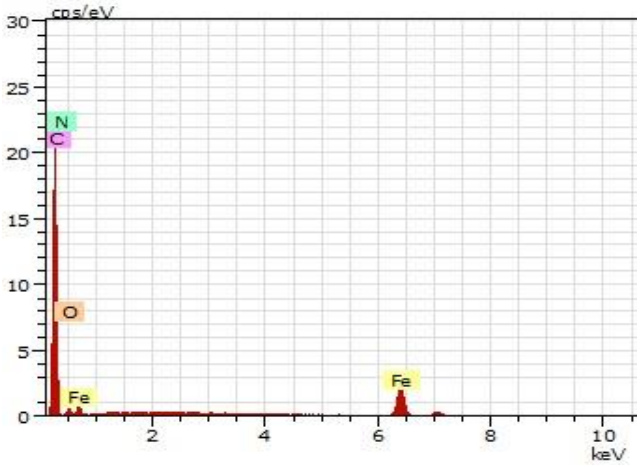

Fig. 3 EDS graph of as-grown CNT using iron as catalyst at 850°C

A clear view of the length and alignment of as grown CNT is shown from Fig 4 to Fig.6.

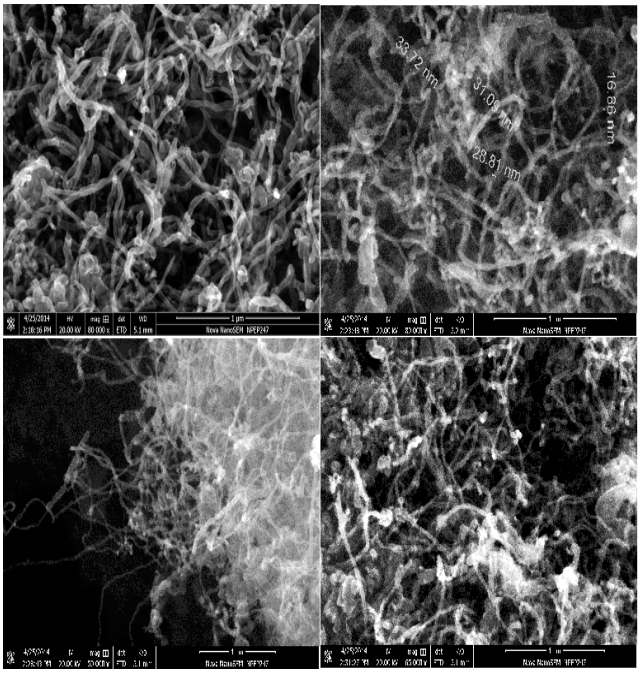

Fig 4: SEM images of carbon nanotubes synthesized by the catalytic decomposition of acetylene using Iron-containing catalyst at 850°C at different magnification. SEM image shows a large number of individual well-graphitize carbon nanotubes growth for Iron as catalyst.

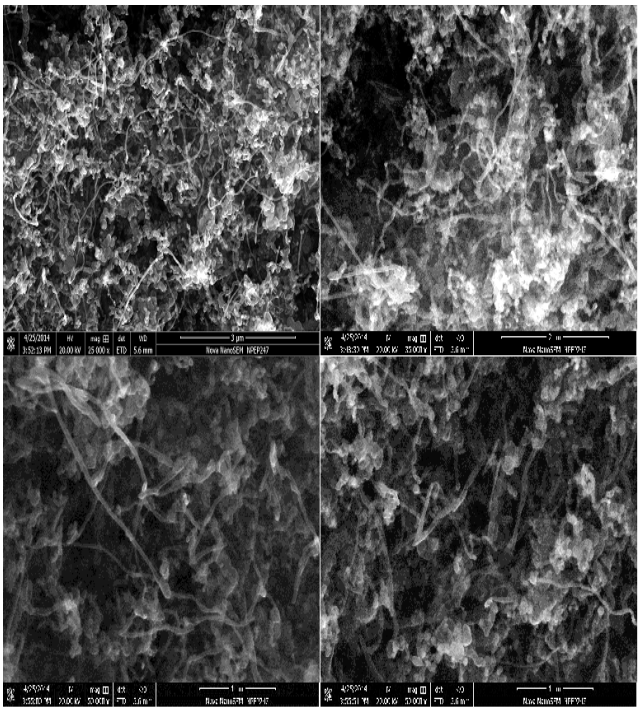

Fig 5: SEM images of carbon nanotubes synthesized by the catalytic decomposition of acetylene using Cobalt-containing catalyst at 850 °C at different magnification. SEM image shows few number of carbon nanotubes.

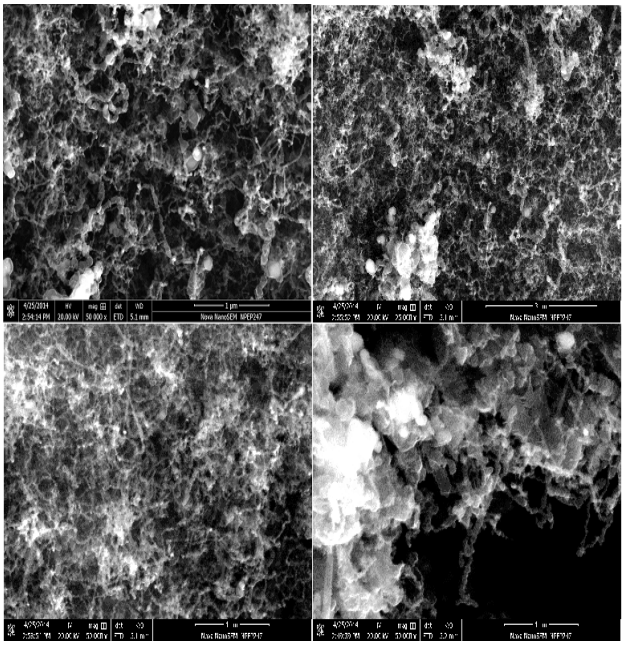

Fig 6: SEM images of carbon nanotubes synthesized by the catalytic decomposition of acetylene using Nickel-containing catalyst at 850°C at different magnification. Very few carbon nanotubes of size 3-4 µm were formed for the catalyst Nickel.

Fig. 4. to Fig. 6. shows SEM micrographs of as-grown CNTs at 850°C on Si substrate for growth time 30 min by using three different metal catalysts (i.e. Iron, Cobalt and Nickel). Arrays of carbon nanotubes were grown for iron as catalysts (Fig. 2) and very few nanotubes of small size were grown when Nickel is used as catalyst. SEM results indicate the high growth of carbon nanotubes, when iron is used as catalyst as compared to other catalyst used at growth temperature 850 °C.

Fig. 7. [(a) to (c)] illustrates the TEM images of the deposited CNTs synthesized for different catalysts.

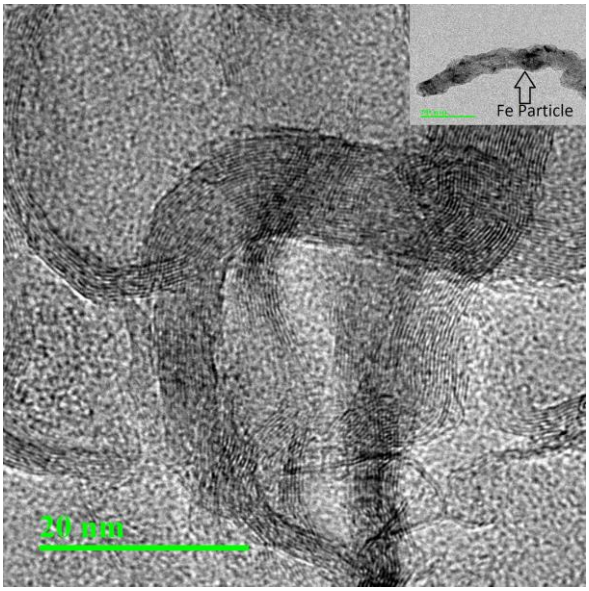

Fig 7(a):- TEM micrograph of individual nanotubes grown at 850°C with a 100 mM iron solution

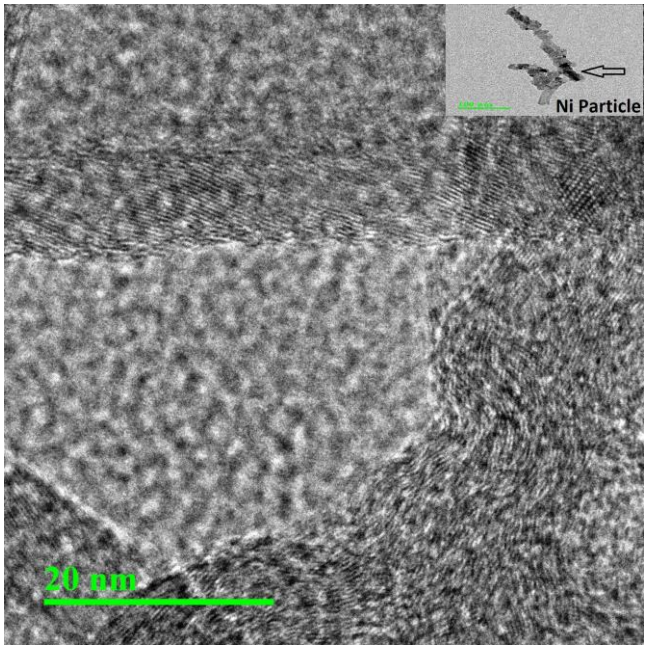

Fig 7(b):- TEM micrograph of individual nanotubes grown at 850 C with a 100 mM nickel solution

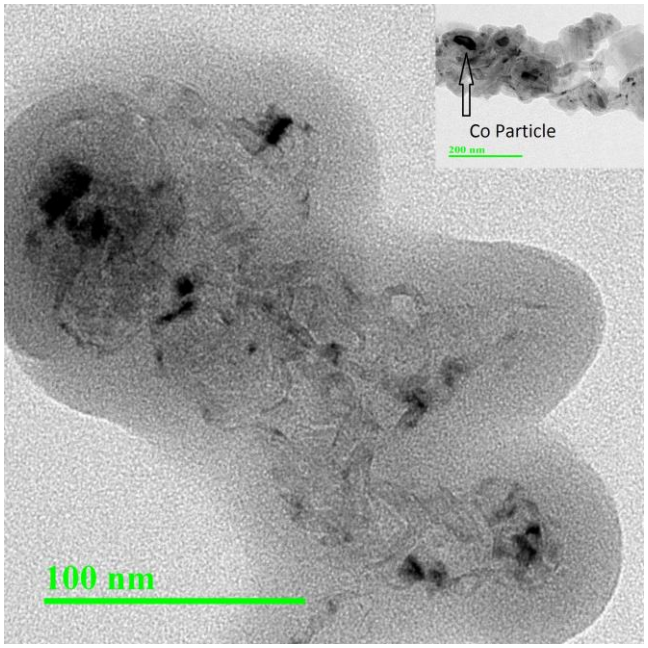

Fig 7(c):- TEM micrograph of individual nanotubes grown at 850°C with a 100 mM cobalt solution.

4. Discussion

The mechanism of the catalytic growth of carbon nanotubes is found similar to the one described by Kanzow *et al* [26]. The key parameters in nanotube CVD growth are the hydrocarbons, transition metal catalyst and growth temperature. At high temperature hydrocarbon gas dissociate under the catalytic effect of transition metal nanoparticles. The carbon particles dissolute and saturates in the metal nanoparticles in the form of carbon nanotube.

Here in this experiment, Acetylene was dissociated catalytically into carbon and Hydrogen. The resulting hydrogen H_2 gas was removed by the vent of CVD. The carbon diffuses into the metal-particle. At high temperature, from the saturated metal particles, precipitation of carbon takes place which leads to the formation of tubular carbon cross-sections in sp^2 structure. Tubular structure is formed in order to avoid the dangling bonds [18]. In the present study Tip-growth mechanism is responsible for carbon nanotubes synthesis, as small elongated catalyst particles were found out at the tip of as-synthesized CNTs as shown in SEM results.

In order to determine the structure and catalyst composition in CVD output XRD technique is used. XRD spectra (Fig. 2) indicate the presence of carbon nanotubes in CVD output with some impurities like catalyst particle, amorphous carbon, silicon particles etc. The strong peak at 26.54° in XRD spectra confirmed relatively good crystallinity of carbon nanotubes and less percentage of amorphous carbon. The EDXA analysis (Fig 3) gives percentage yield (by area) of CNT around 90% when Iron is used as catalyst. In this paper effect of catalyst solutions containing iron, cobalt and nickel on nanotube growth is analyzed and compared. Fig. 4 shows a relatively large number of individual well-graphitized carbon nanotubes of larger size and small diameter were synthesized when Iron is used as catalyst in CVD process. The synthesized nanotubes are highly curved, randomly oriented, have small diameter ranging from 10 to 60 nm. Few nanotubes having length up to a few micrometers ≈50μm and diameter of ≈13nm were found when iron is used as catalyst. We found large clusters of catalyst particles and few nanotubes of large diameter and small size, when Nickel and Cobalt are used as catalysts. It can be seen from Figure 4 to Figure 6 that CNT growth was more for Iron as catalyst as compared to Cobalt and Nickel when used as catalysts. This may be due to several facts. This may be caused by uneven dispersion of catalyst particles. But in our case, catalysts are first reduced from the metal oxide into pure metal-particles before the growth under the flow of Hydrogen gas. And carbon has different solubility in these three metals catalyst at high temperature. The limit of carbon solubility in metal particles is determined by the growth temperature and metal particle size [21, 23]. Due to weak interaction between substrate and Nickel particles, large clusters of Nickel were formed under the flow of Hydrogen gas at high temperature. Larger particles are inactive and don't participate in the CNT growth, but can participate in the production of amorphous carbon. So, a few small branches of carbon nanotubes of small size were seen from figure 6 for Nickel catalyst. Many other groups found large density of nanotubes using Nickel [24, 27] and Cobalt [25].

From the SEM images it can also be seen that the dimensions of the catalyst particles determine the diameter and structure of nanotubes grown in the CVD process [18, 21]. Also, the dimensions of the tubes vary considerably for three catalysts. This is attributed to the large variation of the sizes of catalyst nanoparticles formed on the surface.

From the TEM analysis (Fig. 7), it is clear that there is a close correlation between size of the catalyst particles and diameter of as-synthesized nanotubes. The three catalyst particles i.e. iron, nickel and cobalt were enclosed in the synthesized carbon nanotubes shown in the close-up image, as marked with arrow. However, in analysis of TEM images many nanotubes are observed with no enclosed catalyst particles. From TEM images it was revealed that well graphitized carbon nanotubes having less number of layers were grown when iron is used as catalyst. On the other hand, carbon nanotubes grown for cobalt and nickel catalysts have defects and have low crystallinality. Nanotubes grown for cobalt and nickel catalysts has more number of layers as compared to nanotubes grown for iron catalyst as shown from TEM images.

5. Conclusions

In this paper a significant influence of catalyst material on the quality of the carbon nanostructures is observed, analyzed and compared. Under the studied conditions, Iron is best catalyst as compared to Cobalt and Nickel. High density of carbon nanotubes growth with Iron as catalyst at 850°C is observed. Also, it can be observed that the diameter and structures of nanotubes depend on many parameters such as the thin film thickness, operating temperature and duration of the thermal processing, catalyst used and its composition and so on. In order to improve the quality and yield of carbon nanotubes flow of Hydrogen as is made for longer time. As a weak oxidizer Hydrogen gas helps in reducing amorphous carbon. The synthesis of carbon nanotubes can be further improved by variation in the thickness of thin film of Iron as catalyst deposited on the substrate.

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References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brian, R.F. Curl, R.E.Smalley, Nature, **318**, 162 (1985)
[2] S.Iijima, Nature, **354**, 56 (1991).
[3] D.Ugarte, Nature, **359,** 670 (1992)
[4] S.Iijima, M.Yudasaka, R. Yamada, S. Bandow et al Chem. Phys. Lett. **309,** 165 (1999)
[5] T.W.Odom, J.L.Huang, P.Kim, C.M.Lieber Nature **391,** 62 (1998).
[6] B. Vigolo, A. Penicaud, C.Coulon, C.Sauder, R. Pailer, C. Journet, P. Bernier, P. Poulin, Science **290,** 1331 (2000).

[7] J. L. Hutchison; N. A. Kiselev; E. P. Krinichnaya; A.V. Krestinin; R.O. Loutfy; A.P. Morawsky; V.E. Muradyan; E.D. Obraztsova; J. Sloan; S.V. Terekhov; D.N. Zakharov, Carbon, **39**, 761 (2001).
[8] Y. Saito, T. Nakahira, S. Uemura, J. Phys. Chem. B, **107**, 931 (2003).
[9] M. Kusaba, Y. Tsunawaki, Thin Solid Films, **506–507**, 255 (2006).
[10] N. Braidy, M.A. El Khakani, G.A. Botton, Chem. Phys. Lett., **354**, 88 (2002)
[11] V. Ivanov, A. Fonseca, J.B. Nagy, A. Lucas, P. Lambin, D. Bernaerts, X.B. Zhang, Carbon, **33**,1727 (1995).
[12] Z.F. Ren, Z.p.Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science, **282,** 1105 (1998)
[13] C. J. Lee, D. W. Kim, T. J. Lee, Y. C. Park, Y. H. Lee, W.B. Choi, N.S. Lee, G.S. Park, J.M. Kim Chem. Phys. Lett **312,** 461 (1999)
[14] Y.C. Choi, D.J. Bae, Y.H. Lee, B.S. Lee, I.T. Han, W.B. Choi, N.S. Lee, J.M. Kim Syn. Met., **108,** 159 (2000).
[15] N. M. Rodriguez, J. Mater. Res., **8,** 3233 (1993)
[16] M. Nath, B.C. Satishkumar, A. Govindaraj, C.P. Vinod, C.N.R. Rao, Chem. Phys. Lett. **322**, 333 (2000).
[17] Rümmeli et al. Nanoscale Research Letters, **6**, 303 (2011)
[18] M. Kumar, Y. Ando, Journal of Nanoscience and Nanotechnology **10**, 3739 (2010).
[19] K. Koziol et al., Synthesis of Carbon Nanostructures by CVD Method, Adv Struct Mater 5, DOI 10.1007/8611_2010_12. (2010)
[20] G Y Xiong, Y Suda, D Z Wang, J Y Huang, Z F Ren Nanotechnology **16**, 532 (2005)
[21] A. Moisala, A.G. Kauppinen, E.I. J. Phys.: Condens. Matter., **14,** 3011 (2003).
[22] Xiuyun Zhang, Lu Wang, John Xin, Boris I. Yakobson, Feng Ding, J. Am. Chem. Soc. Doi: 10.1021/ja405499x. (2014),
[23] Arnaud Magrez, Jin Won Seo, Rita Smajda, Marijana Mionic, Laszlo Forro, Materials, **3**, 4871 (2010).
[24] S.A. Moshkalyova, A.L.D. Moreaub, H.R.Guttie´rrezb, M.A. Cottab, J.W. Swarta Materials Science and Engineering B **112**, 147 (2004)
[25] F. Taleshi, International Nano Letters, **2**, 23 (2012)
[26] H. Kanzow, A. Schmalz, A. Ding, Chem. Phys. Lett., **295,** 525 (1998)
[27] C.Klinke, J.M.Bonard, K. Kern, Surface Science, **492**, 195 (2001).
[28] V. Jourdain, C. Bichara, Carbon, **58**, 2 (2013)

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