Synthesis and Study of Applications of Metal coated Carbon Nanotubes

[1]Sandeep Mani Tripathi and [2]Tiwari Sushil Bholanath*

Department of Electronics and Communication Engineering, SRM University
Katttankulathur, Chennai-603203.
*[1]sandy.sandeep07@gmail.com, [2]sashisrmist09@gmail.com**

Abstract

In this project, we have studied the growth, morphology and surface characterization of metallized Carbon Nanotubes and conducted a comprehensive study on the application of this technology. Carbon Nanotubes are a tubular shaped isotope of carbon with unique physical, chemical and mechanical properties. In particular, we synthesized Carbon Nanotubes, using a RF-Powered Plasma Enhanced Chemical Vapor Deposition System. In this process, we used methane as the carbon source and high purity argon gas to create the plasma. The Silicon (Si)/Glass (SiO_2) substrate was coated with a transition metal as a catalyst using both wet chemical means and Electron beam Evaporation.

After successfully growing Carbon Nanotubes, they were metallized with Iron (Fe) Nanoparticles using Physical Vapor Deposition System with an E Beam Evaporator. A comparative study between the metal coated and non coated Carbon Nanotubes was conducted. Possible applications such as use of this technology in synthesis of FET's, use as Scanning Probe Microscope tips and other electronic applications are also discussed. A successful development in this field would have enormous applications in various fields and could lead to fabrication of miniature electronic components (in the order of nanometers).

Keywords: *PECVD, PVD, Metalized SWCNT, NANO FET, XRD.*

1. Introduction

In 1991, S.IIjima discovered Carbon Nanotubes by chance during investigation of fullerene production. Since then, Carbon Nanotubes have attracted the immense interest among the researchers and has been the focus of many research projects. Its unique properties such as its chemical inertness, its physical properties such as its electrical conductivity, tensile strength, flexibility, elasticity and thermal conductivity make it a material that can be used in a variety of applications. Ever since the discovery of the Carbon Nanotubes in early 1990s the scientists have actively been exploring the properties of the material with astounding results. The potential applications of Carbon Nanotubes in electronics are a topic of research that has generated significant interest and attention from the International Scientific Community. Despite having found several interesting properties and potential application Carbon Nanotubes are yet find a technological market significance because of limited availability of methodologies of reliably synthesizing Carbon Nanotubes with good percentage yield and consistent physical and chemical properties. It is a well known fact that much of the Carbon Nanotubes produced are usually formed along with a mixture of amorphous carbon, fullerenes and other impurities. Cost effective and efficient ways of separation and filtration of Carbon Nanotubes are yet to be discovered. Amongst the available methodologies the three most commonly used techniques includes Arc–Discharge method, Laser Ablation method and Chemical Vapor Deposition (CVD). Of these the CVD has proved to be a comparatively reliable way of synthesizing CNT's.

For the purposes of our project we have concentrated on a modified version of the CVD known as Plasma Enhanced Chemical Vapor Deposition. Carbon Nanotubes can be metallic and semi-conducting based on the physical structure of the Carbon Nanotube. For the course of this project, we have synthesized Carbon Nanotubes using Plasma Enhanced Chemical Vapor Deposition and then coated the CNT's with Iron (Fe) using Electron Beam Physical Vapor Deposition. The main purpose of doing so involves exploiting the size and morphological properties of the CNTs while ensuring that the structure as a whole is conducting in nature. This conformity in electric properties has significant applications in the field of electronics.

2. Objective

The main objective of this project is to study the growth and morphology of Carbon Nanotubes synthesized using the aforementioned techniques. The highlight of this work is the coating of the synthesized Carbon Nanotube with a conducting metal such as Iron to enhance it's electrically properties thereby creating a Nanotube with a definitive current carrying ability. The surface characteristics and the dimensions of the Carbon Nanotube were also analyzed.

It is a well documented fact that the main problem with application of Carbon Nanotubes in electronics is primarily because the methodology synthesis of Carbon Nanotubes and there is no way to reliably create large volumes of Carbon Nanotubes with consistent electrical properties. By coating the synthesized Carbon Nanotube with a conducting metal we can ensure that all the Carbon Nanotubes have similar electrical properties though their structural and physical properties may vary.

The work was divided into several modules which included:

- Substrate preparation
- Coating of a transition element catalyst
- Growing of Carbon Nanotubes
- Analysis of the Carbon Nanotubes
- Coating with a conducting metal (Fe)
- Analysis of the resultant metal coated Carbon Nanotube

3. Review of Literature

Since the discovery of carbon nanotubes by Iijima [1], carbon nanotubes (CNTs) have attracted much attention in various fields, owing to their unique mechanical and electrical properties. They have been considered to be candidates for various applications such as catalysts [2], nanoscale electronic systems [3], and gas storage materials [4]. However, it has also been recognized that the modified CNTs will improve their properties and broaden their applications [5]. So far, several methods have been reported to coat carbon nanotubes, such as electroless plating methods [6,7], physical vapor deposition [8], atomic-layer deposition in a binary reaction sequence [9] and so on [10,11], which hold promise in applications such as catalysts, sensors, semiconductor devices and new reinforced materials.

Magnetic nanocomposites have potential applications in various areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging. Therefore, studies on magnetic nanocomposites, especially on magnetic carbon nanotubes (CNTs), are rapidly expanding. Recently, Kozhuharova and co-workers synthesized aligned Fe–Co alloy-filled MWCNTs on silicon substrates via the pyrolysis of ferrocene/cobaltocene mixtures [12]. Stoffelbach and co-workers decorated MWCNTs with magnetic nanoparticles by adding a solution of positively charged Fe_3O_4 nanoparticles to the negatively charged MWCNTs [13]. Korneva proposed a new method to produce magnetic tubes by filling MWCNTs with ferrofluid [14]. Sun fabricated magnetic carbon nanotube composites by the decomposition of ferrocene on MWCNTs at different temperatures [15]. Various magnetic materials including iron [16], iron oxide [17], nickel [18], cobalt [19], $CoFe_2O_4$ [20] and FeCo [21] encapsulated in CNTs have been prepared. However, it is still difficult to uniformly modify CNTs with accessible cavities, which is essential for applying magnetic carbon nanotube composites in cellular delivery systems [22].

Generally, CNTs are used as templates for producing new one-dimensional materials due to their morphology and scale, such as filling CNTs with metals, metal oxidation, and C60 using chemical techniques [23], surface-coating or surface-adsorbing SnO2 using a one-step wet chemical method [24,25], SiC using chemical vapor deposition(CVD) [26],Co–B using chemical reduction method [27], CdSe via amide bond formation [28],Ti, Ni, Pd, Al, Fe, Au using electron-beam deposition [29], Cu and Ni using electroless plating method [30]. However, up to now, CNTs coated with Fe using Electron Beam Evaporation have not been reported. The closest is the coating of Iron Oxide Nanoparticles on Carbon Nanotubes using methanol-thermal reaction by Huang et al.

4. Methodology

As previously mentioned, the entire work of this project was divided into six modules or phases which we shall now discuss in detail

- Substrate preparation
- Coating of a transition element catalyst
- Growing of Carbon Nanotubes
- Analysis of the Carbon Nanotubes
- Coating with a conducting metal (Fe)
- Analysis of the resultant metal coated Carbon Nanotube

Two substrates were chosen for the experimentation procedures. One was a polished Silicon (100) substrate while the other was a Glass substrate. Both were washed thoroughly using a 3:1 mixture of HNO_3: HCl before being cleaned using Millipore Deionized water. After drying, they were further cleaned using Acetone as a cleaning agent to improve all impurities.

After this the substrate was coated with a metal catalyst to enhance the growth of Carbon Nanotubes. This was done by two methods namely Wet Chemical and Electron Beam Evaporation. The former method involved taking 15mg of Analytical Grade Ferric Nitrate obtained from SRL Pharma was dissolved in 100ml of 2-Proponol which was also obtained from SRL Pharma. Few drops of this mixture was then put on the substrate and rinsed with Hexane. The coating was then made uniform by placing it in an Apex Instrument's Spin Coating and spinning at 6000rpm for 120secs. The latter method involved placing the substrate in Hindhivac's Physical Vapor Deposition Unit and pumping the chamber down to $5x10^{-7}$mbar. This was done using a combination of Rotary Pump and Turbomolecular Pump. The Iron granules were procured from Alfa Aesar and the evaporation was done at the rate of 0.1Å per second. A total of 50Å were thus deposited. Characterization studies were conducted using an Aligent Technologies' Scanning Probe Microscope for characterization studies and Panalytical's X-Ray Diffractometer for elemental analysis.

After deposition of catalyst, the substrate was placed in Hindhivac's Plasma Enhanced Chemical Vapor Deposition for Carbon Nanotube growth. The chamber was pumped down to $4x10^{-6}$ mbar using a combination of Diffusion Pump and Rotary Pump. The RF Power (Frequency 13.6MHz) of the system was switched on ionizes the Argon gas which is introduced into the chamber thereby creating plasma. The substrate heater was used to heat the substrate to a temperature of 550°C to enhance the growth of Carbon Nanotubes. The power was maintained at 200 W. The Argon:Methane gas ratio was kept at 5:1 using the mass flow controller. The glow discharge which was obtained was kept stable for 20mins to aid the growth and nucleation of Carbon Nanotubes.

The substrate was then removed from the PECVD and analyzed using Ajilent Technologies' Atomic Force Microscopy, Shimadzu's Fourier Transform Infra Red Spectroscopy and Perkin Elmer's Raman Spectoscopy to confirm the presence of Carbon Nanotubes.

After analysis, the substrate was again placed in the Physical Vapor Deposition and the deposition of Iron on top of the grown Carbon Nanotube was carried out in a fashion similar to the coating of catalyst. But, in this case 150Å of Fe was deposited to ensure connectivity which ensures conductivity. Then, the substrate was removed from the Physical Vapor Deposition and X-Ray Diffraction Studies were conducted to confirm the presence of Carbon Nanotubes coated with Fe.

5. Finding and Analysis

Fig 1 shows typical images of Iron Nanoparticles synthesized using Wet Chemical methods mentioned before. The substrate was found to be heavily coated with Iron Nanoparticles

Figure 1. AFM Image of Iron Nanoparticles

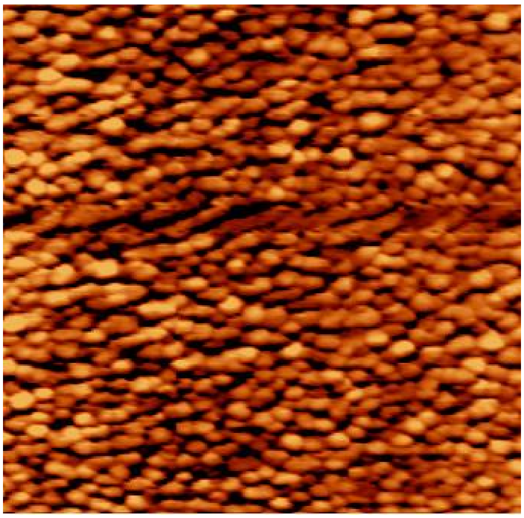

Figure 2. AFM Image of Iron Nanoparticles

Figure 2 shows typical images of Iron Nanoparticles synthesized using Electron Beam Physical Vapor Deposition. The substrate was found to be heavily coated with well aligned Iron Nanoparticles. The post annealing which was performed at 500°C for two hours allowed for a uniform nucleation and growth of the Iron Nanoparticles. Fig 3 shows the X-Ray Diffractometer pattern which confirms the presence of Iron Nanoparticles. The readings were taken using a Panalytical X-Ray Diffractometer.

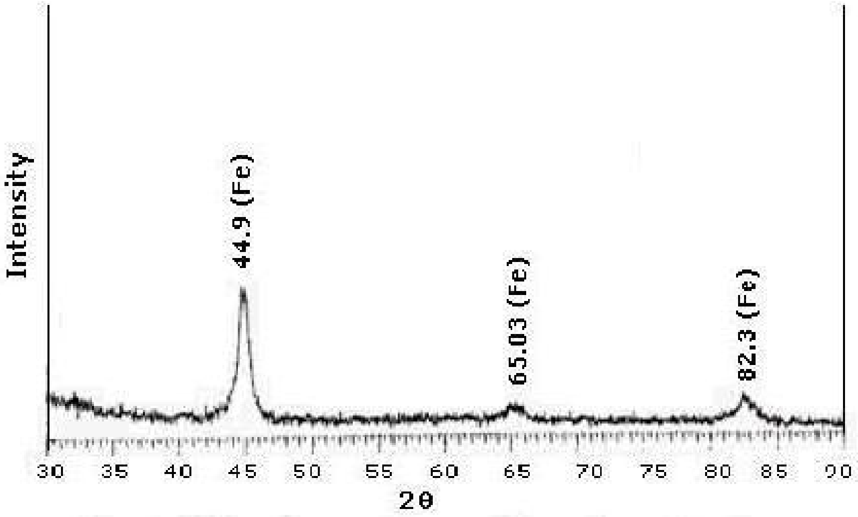

Figure 3. X-Ray Diffractometer pattern of Iron Nanoparticles.

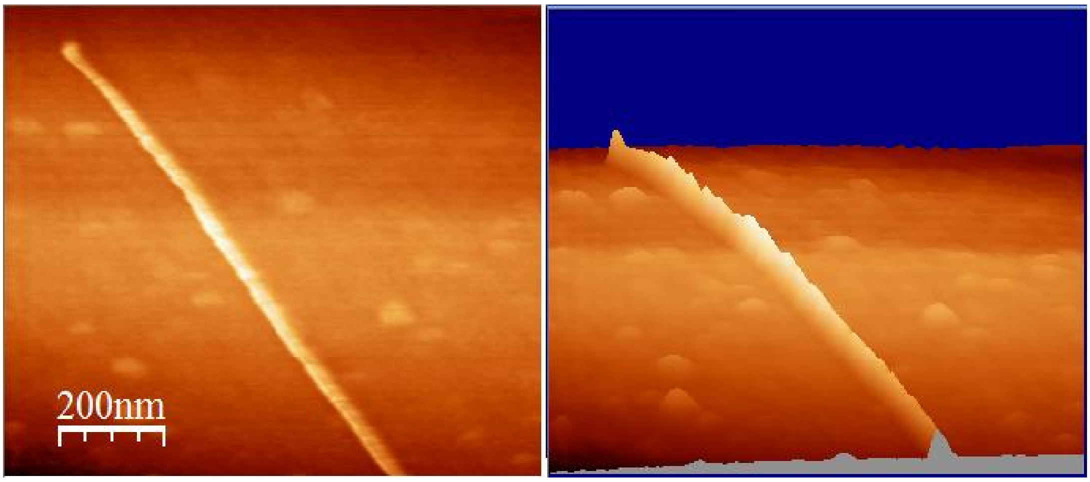

Figure 4. 2D and 3D AFM images of Carbon Nanotube grown on Si (100)

Figure 4 and 5 shows AFM images of Carbon Nanotubes synthesized using Plasma Enhanced Chemical Vapor Deposition. The image clearly shows the growth of distinct Carbon Nanotubes along with impurities such as amorphous carbon, fullerenes and other isotopes of carbon. The tubes were found to be of diameter approximately 100nms as shown by the corresponding line profile. This shows a good consistent match with the sizes of the catalyst Iron Nanoparticles and is a clear indication that the Iron Nanoparticles were instrumental in the growth of these Carbon Nanotubes.

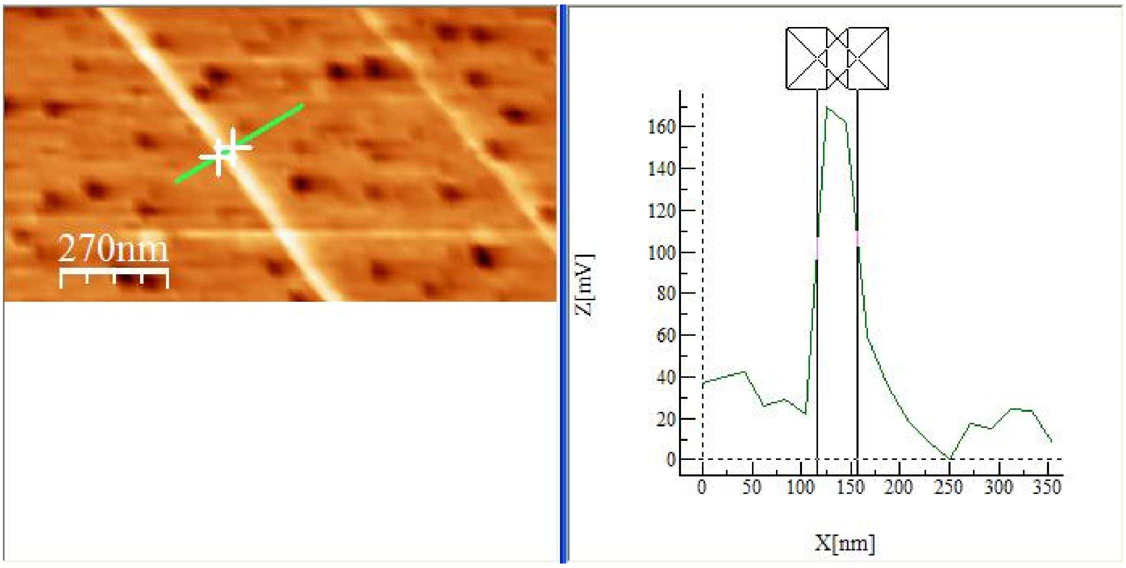

Figure 5. AFM Image and Line Profile of Carbon Nanotubes

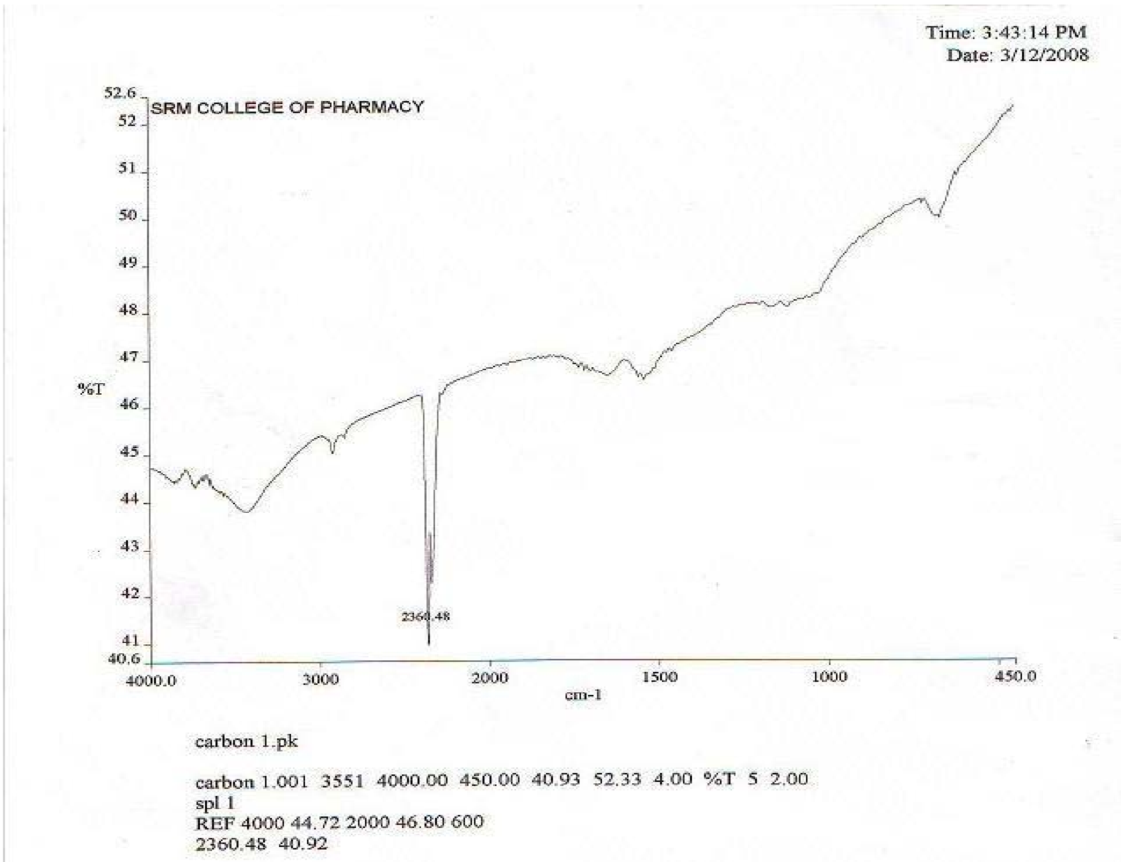

Figure 6. FTIR Spectrum of Carbon Nanotubes

Fig 6 shows a FTIR reading of the synthesized Carbon Nanotubes which was obtained from a Shimadzu's FTIR Spectroscopy from SRM College of Pharmacy. The image clearly shows the presence of carbon thereby giving us an indication of the presence of Carbon Nanotubes. Fig 7 shows a Raman Spectroscopy reading taken for the same sample of Carbon Nanotube. The Raman spectrum was measured, to confirm the carbon nanostructures in the sample. The resonant Raman spectrum of carbon nanostructures shows two main features: radial breathing mode (RBM) band and G band. The Raman spectrum indicates that quite a few disordered carbon phases exist. That is the result of a substantial amount of amorphous carbon.

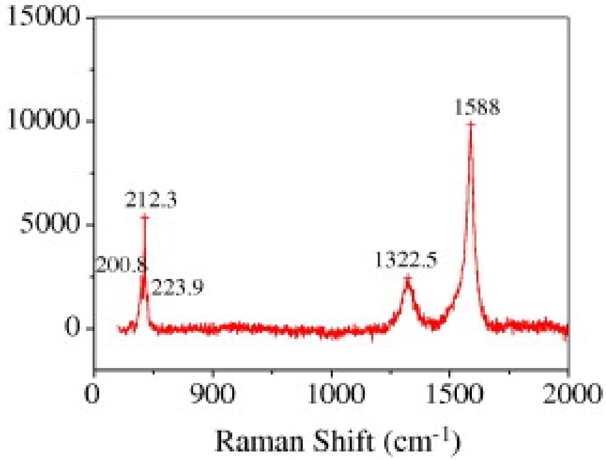

Figure 7. Raman Spectra of synthesized Carbon Nanotubes

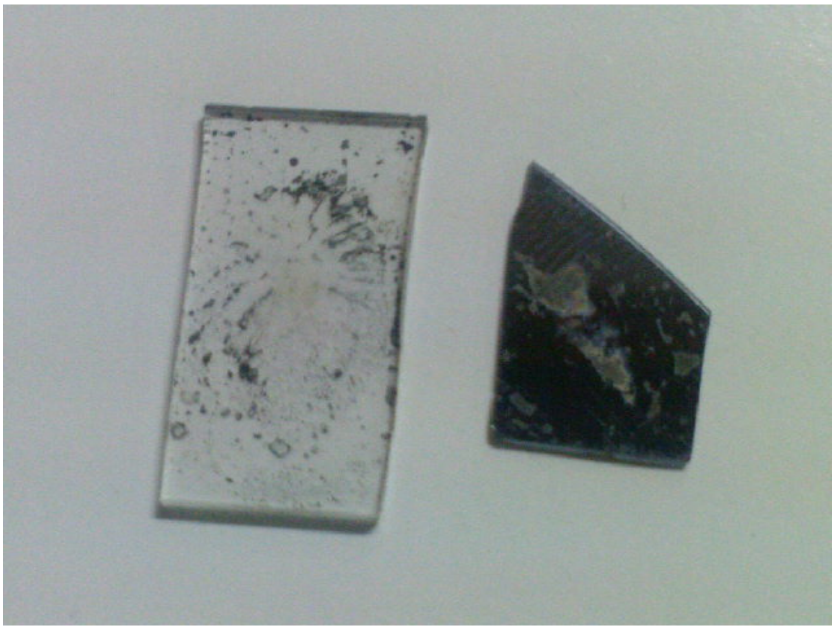

Figure 8. Glass and Si (100) substrates with a characteristic black coating containing Carbon Nanotubes

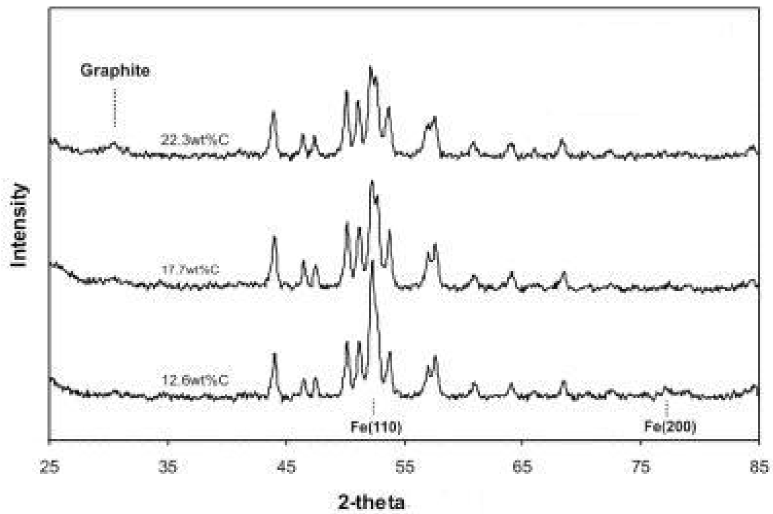

Figure 9. X ray Diffractometer patterns of Iron Coated Carbon Nanotubes

Fig 8 shows the Si(100) and Glass substrates with a characteristic black coating of carbon containing Carbon Nanotubes. Fig 9 shows the X Ray Diffractometer readings of metallized carbon nanotubes showing the presence of carbon as well as iron. The non marked peaks are attributed to the presence of Fe_2C. The reading was taken using a Rigaku X-Ray Diffractometer.

6. Conclusions

This work categorically proves that Carbon Nanotubes can be successfully synthesized using Plasma Enhanced Chemical Vapor Deposition with the help of a transition element catalyst. Further, it shows that the metallization of carbon nanotube is feasible by a simple evaporation process leading to metallic nanotube with reliable electrical and magnetic properties. This study demonstrates the successful development of a simple component which has crucial applications in the fields of Electronics and Material Science.

7. Implication/Application:

The basic implication of this work is in fabricating carbon nanotubes with reliable properties in a consistent fashion. This indicated that the reliability issue that has been plaguing the commercialization of carbon nanotube technology from the day of its discovery can finally be gotten rid of to a certain extent. Further, the product that is resultant can be used in many innovative ways to enhance the properties of carbon nanotubes. The technology arising from this work has potential applications in many fields.

- The metallized carbon nanotubes can be used as highly sensitive Scanning Tunneling Microscope and Magnetic Force Microscope tips.
- Can be used as interconnects or wires in a number of electronic applications including the fabrication of FET's.
- Has a potential application in fabrication of magnetic recording devices.
- The method can be extended to coat different metal to obtain a nanosized tubular structure with high current carrying capacity.
- The magnetic properties of the metals can also be exploited in various ways at the nanometer scale.

8. Limitation

- Reliable growth of carbon nanotubes with similar properties is very difficult.
- Formation of impurities such as amorphous carbon, fullerenes and other carbon compounds and isotopes during the synthesis of carbon nanotubes creates significant problem with the purity and reliability of the synthesized Carbon Nanotubes.
- The accurate placement and growth of Carbon Nanotube is extremely difficult without the use of Lithography Tools. Hence, there is an issue when we want to synthesize reliable nanodevices.
- The technology can have severe drawbacks if the metallization of the carbon nanotube is not continuous and hence conducting.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] Z.J. Liu, Z. Xu, Z.Y. Yuan, D. Lu, W. Chen, W. Zhou, Catal. Letters 72 (2001) 203.
[3] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, Science 278 (1998) 100.
[4] A.C. Dillon, K.M. Jones, T.A. Bekkendahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[5] H. Kim, W. Sigmund, Appl. Phys. Lett. 81 (2002) 2085.
[6] F.Z. Kong, X.B. Zhang, W.Q. Xiong, F. Liu, W.Z. Huang, Y.L. Sun, J.P. Tu, X.W. Chen, Surf. Coat. Technol. 155 (2002) 33.
[7] L.M. Ang, T.S.A. Hor, G.Q. Xu, C.H. Tung, S.P. Zhao, J.L.S. Wang, Carbon 38 (2000) 363.
[8] Y. Zhang, Q. Zhang, Y. Li, N. Wang, J. Zhu, Solid State Commun. 115 (2000) 51.
[9] J.S. Lee, B. Mina, K. Cho, S. Kim, J. Park, Y.T. Lee, N.S. Kim, M.S. Lee, S.O. Park, J.T. Moon, J. Cryst. Growth 254 (2003) 443–448.
[10] Z. Liu, Z. Xu, Z. Yuan, W. Chen, W. Zhou, L. Peng, Mater. Lett. 57 (2003) 1339.
[11] X.W. Wei, X.J. Song, J. Xu, Y.H. Ni, P. Zhang, Mater. Chem. Phys. 92 (2005) 159.
[12] R. Kozhuharova, M. Ritschel, D. Elefant, A. Graff, I. Monch, T. Muhl, C.M. Schneider, A. Leonhardt, Journal of Magnetism and Magnetic Materials 290 (2005) 250.
[13] F. Stof felbach, A. Aqil, C. Jerome, R. Jerome, C. Detrembleur, Chemical Communications 36 (2005) 4532.
[14] G. Korneva, H.H. Ye, Y. Gogotsi, D. Halverson, G. Friedman, J.C. Bradley, K.G. Kornev, Nano Letters 5 (2005) 879.
[15] Z.Y. Sun, Z.M. Liu, Y. Wang, B.X. Han, J.M. Du, J.L. Zhang, Journal of Materials Chemistry 15 (2005) 4497.
[16] S. Karmakar, S.M. Sharma, M.D. Mukadam, S.M. Yusuf, A.K. Sood, Journal of Applied Physics 97 (2005) (054306-1).
[17] B.K. Pradhan, T. Toba, T. Kyotani, A. Tomita, Chemistry of Materials 10 (1998) 2510.
[18] J.C. Bao, Q.F. Zhou, J.M. Hong, Z. Xu, Applied Physics Letters 81 (2002) 4592.

[19] R. Kozhuharova, M. Ritschel, D. Elefant, A. Graff, A. Leonhardt, I. Monch, T. Muhl, S. Groudeva-Zotova, C.M. Schneider, Applied Surface Science 238 (2004) 355.
[20] C. Pham-Huu, N. Keller, C. Estournes, G. Ehret, M.J. Ledoux, Chemical Communications 17 (2002) 1882.
[21] A.L. Elias, J.A. Rodriguez-Manzo, M.R. McCartney, D. Golberg, A. Zamudio, S.E. Baltazar, F. Lopez-Urias, E. Munoz-Sandoval, L. Gu, C.C. Tang, D.J. Smith, Y. Bando, H. Terrones, M. Terrones, Nano Letters 5 (2005) 467.
[22] J. Miyawaki, M. Yudasaka, H. Imai, H. Yorimistu, H. Isobe, E. Nakamura, S. Iijima, Advanced Materials 18 (2006) 1010.
[23] M. Monthioux, Carbon 40 (2002) 1809.
[24] L.P. Zhao, L. Gao, Carbon 42 (2004) 1858.
[25] W.Q. Han, A. Zettl, Nano Lett. 3 (2003) 681.
[26] Y. Morisada, Y. Miyamoto, Mater. Sci. Eng., A 381 (2004) 57.
[27] Z.J. Liu, Z.D. Xu, Z.Y. Yuan, W. Zhou, L.M. Ping, Mater. Lett. 57 (2003) 1339.
[28] J.M. Haremza, M.A. Hahn, T.D. Krauss, Nano Lett. 2 (2002) 1253.
[29] Y. Zhang, N.W. Franklin, R.J. Chen, H. Dai, Chem. Phys. Lett. 331 (2000) 35.
[30] L.M. Ang, T.S.A. Hor, G.Q. Xu, C.H. Tung, S.P. Zhao, J.L.S. Wang, Carbon 38 (2000) 363.

Authors

[1]**Sandeep Mani Tripathi,** Undergraduate student Department of ECE at SRM University, Chennai-INDIA. Working in the SRM Nano-satellite project on the communication subsystems. Fields of interest are Nano electronics, digital design, Image processing, Space Science. Received best paper Award for Technologically Significant Advance in Research and Development for contributions in the fields of miniaturizing the electronics components in IIT KANPUR.

[2]**Tiwari Sushil Bholanath*,** Under-Graduate student Department of Electronics and communication Engineering SRM University, Chennai India. A researcher at NRC SRM University. My research is focused on the nanoelectronics and development of advanced technologies for the miniaturizations of the electronics components for the efficient uses. Worked for the defense project for the Bharat electronics ltd, INDIA. Fields of interest are the nano electronics, embedded system design, wireless communications. Received best paper Award for Technologically Significant Advance in Research and Development for contributions in the fields of miniaturizing the electronics components in IIT KANPUR.