



Fabrication of Carbon Based Nanostructured Materials on Si/SiO₂ Substrate and Their Growth Mechanism over Different Catalysts

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Abstract

In this study, carbon based nanostructured material was synthesized by catalytic chemical vapor deposition (CCVD) technique using metallic (Ni, Co) and Semiconductor (FeCl₃·6H₂O/ZnO) catalysts on Si/SiO₂ substrates. Acetylene (C₂H₂) and argon were utilized as a precursor and carrier gases respectively. The changes in surface morphology, crystal structure, elemental distribution, surface roughness and crystalline character were observed by scanning electron microscopy (SEM), transmission electron microscope (TEM), energy dispersive x-ray spectroscopy (EDS), atomic force microscopy (AFM) and Raman spectroscopy respectively. The results show the dependence of carbon nanostructured materials growth on Si/SiO₂ substrates using catalysts; Ni, Co and FeCl₃·6H₂O/ZnO found to be in the range of 10-20 min at 900/1100 °C temperature. This study can be fruitfully employed for the fabrication of Nano-sensors.

Keywords: Carbon Nanofibers; Catalysts; Metal-Oxides; Nanocomposites; Raman; Semiconductor; Zno

Abbreviations: CCVD: Catalytic Chemical Vapor Deposition; TEM: Transmission Electron Microscope; SEM: Scanning Electron Microscopy; AFM: Atomic Force Microscopy; EDS: Energy Dispersive X-Ray Spectroscopy; CNT: Carbon Nanotube; PVD: Physical Vapor Deposition.

Introduction

Recently, fabrication of nanomaterials for technological development [1-3] is in trend, which is a clear indication of miniaturization of electronic devices in recent years, not only this technology reduces the size but also, the developed materials have superior performance than the

bulk counterparts. This advancement in performance of the materials is due to small size, which allows electron confinement leading to quantum effects [4]. Nanomaterials have been generating a great interest in; electronics, environmental and medical applications [5-7].

Since the discovery of carbon nanotube (CNT) [8], this material is creating a lot of attention because of its structural, thermal, mechanical, electrical and chemical properties [9]. Long and slender C-C covalently bonded structure with large surface area and hexagonal networking makes CNT a very unique material for various applications. Therefore, CNT's attracts much attention in the field of sensors, actuators,

transistors, and energy storage devices [1]. Moreover, it can also be adopted in the formation of hybrid materials, which makes them promising in optoelectronic, environmental and medical applications [2,6,7].

Considering previous research conducted in the field of CNT fabrication, researchers have found CNT's of different shapes, size and surface morphology depending on their synthesis method, catalyst and carbon source [10-23]. Catalytic chemical vapor deposition (CCVD) is the most commonly utilized technique for CNT production, where transition metals like Ni, Co, Fe or their alloys are used for catalytic decomposition. Talking about the carbon source several sources have been investigated for the production of CNT's in combination with catalyst. At the initial stage of growth, the accumulation of decomposed carbon is totally dependent on the catalyst and the growth temperature [12-17].

The growth of CNT's on Si/SiO₂ substrate is very practical and essential for the optoelectronic devices and environmental applications in sensors, integrated circuits and water purification [18]. Unique characteristics of SiO₂ (stability, temperature resistant, electrical insulator) makes them very important for several applications and well-defined local structure of SiO₂ provides a decent platform for device fabrication.

Different mechanisms proposed for the growth of CNT are based on the reaction conditions are often contradicting on the basis of shape. The influence of the deposition temperature and catalyst used, affects the morphology of the CNT growth on silicon surface, the increase of the temperature for growth of CNT forms a thin to thick nano-worms of which diameter varies between 25 to 1 μm in size [14,18,24-29]. The internal diameter and number of walls formation also depends on the catalyst used as well the gases introduced during growth like H₂, the role of H₂ is to make the reaction rate faster as well as the linear alignment of CNTs. Usually found that the carbon structures grown at higher temperature consists of a nanotube core and an additional layer of amorphous or polycrystalline carbon, which is clearly mentioned by many researchers [11]. Researchers also mentioned that CNT growth is a very fast process and the growth takes place during first 5 minute but the same times found that the quantity of growth at initial stage is quite low as well as also affects the length and shape of grown CNT [10,14,16,19,21,26-29].

Our idea of CNT growth on Si/SiO₂ substrate is to optimize the growth conditions and to choose a better catalytic candidate for the fabrication of optoelectronic and environmentally applicable devices. In this paper we report the growth of carbon nanotubes on metals (Ni, Co)

and semiconductor (FeCl₃.6H₂O/ZnO) catalysts using CCVD technique. CNT growth was performed inside a quartz tube using ultra-pure acetylene (C₂H₂) gas as a carbon source, argon (Ar) as a carrier gas and the growth temperature of 900/1100°C for 10-20 min growth time. The catalysts; Ni and Co were deposited using physical vapor deposition (PVD) technique at nonmetric dimension, while ZnO catalyst was decomposed together with the acetylene flow in the quartz chamber onto Si/SiO₂ substrate coated with FeCl₃.6H₂O by the use of spin coating technique. The flow of carrier gas was constant for all the experiments setups while the oven temperature and precursor flow were varied on the performing experiments.

Experiment

First, Si/SiO₂ substrates were cleaned for removal of organic and metallic contamination from the surface using NH₄OH:H₂O₂:H₂O (1:1:5) at 75°C for 10 min, and washed with deionized (DI) water. Then substrates were immersed and cleaned by HCl: H₂O₂: H₂O (1:1:5) for 15 min for removal of metal particle on the surface and washed several times using DI water and finally spray compressed gas was used to avoid any spot formation.

To enhance the CNT growth on Si/SiO₂ substrate a thin layer of catalyst was plated by applying physical vapor deposition (PVD) technique, which is well studied technique for the formation of homogeneous and fine layer of catalyst. Metal catalysts, Ni, and Co (3 nm thick each) were deposited by applying 28 A and 30 A current respectively in a vacuum chamber. In another step, 10⁻² molar solution of FeCl₃.6H₂O was deposited on silica substrate by applying spin coating technique at 5000 RPM and medium acceleration for 60 sec., which forms around 1 nm layer. For CNT growth, catalyst deposited silica substrate was placed in a quartz tube oven on alumina boat using Argon as a carrier and acetylene as a precursor gas. Here we studied the CNT growth based on three parameters; growth time, growth temperature and catalyst, as shown in table 1. In case of ZnO-CNT composite, growth the ZnO powder was vaporized at 1100°C in quartz tube as the melting point of ZnO is ~1080 °C. Prior to CNT growth, the quartz tube was purged by the flow of Ar gas, 85 sccm for 15-20 minutes then the oven temperature was increased with the flow of Ar. While the temperature reach to the label as mentioned in the table 1 the flow of C₂H₂ gas was introduced in the oven at 5-8 sccm flow rate. Figure 1 show the experimental setup used in our experiments. To maintain the inert environment during the experimental procedure Argon gas supply was kept continuous until the oven temperature gradually decreases to the ambient temperature. The characterization of CNT grown was observed and confirmed by applying XRD, AFM, SEM, EDS, TEM and Raman techniques.

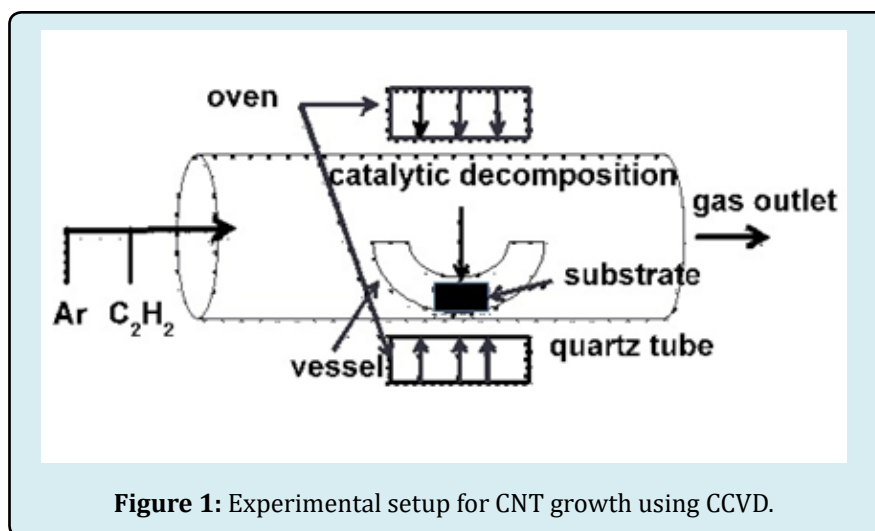


Figure 1: Experimental setup for CNT growth using CCVD.

Results and Discussion

The thickness of the deposited catalyst was found ~ 3 nm by using ellipsometry technique. After catalyst deposition CNT growth was performed in a quartz tube oven at 750–900°C temperature using C₂H₂ (acetylene gas) as a precursor and Ar as a carrier gas (Figure 1). The flow of carrier gas was constant while the oven temperature and precursor flow was varied in the performed experiment. Initially Ar gas was passed for 15 min to make the quartz tube an inert medium,

then the temperature was increased to the desired value. After attaining the desired temperature, acetylene gas was passed in the quartz tube oven for CNT growth as mentioned in the Table 1. Figure 2 shows the atomic force microscopic images of catalytic deposition and CNT growth roughness on the silica substrate. Figure 2a show Ni catalyst roughness on silica substrate about 0.4 nm while after CNT growth the roughness was found 6.2 nm (Figure 2b) while on Co catalyst the roughness was about 166 nm (Figure 2c).

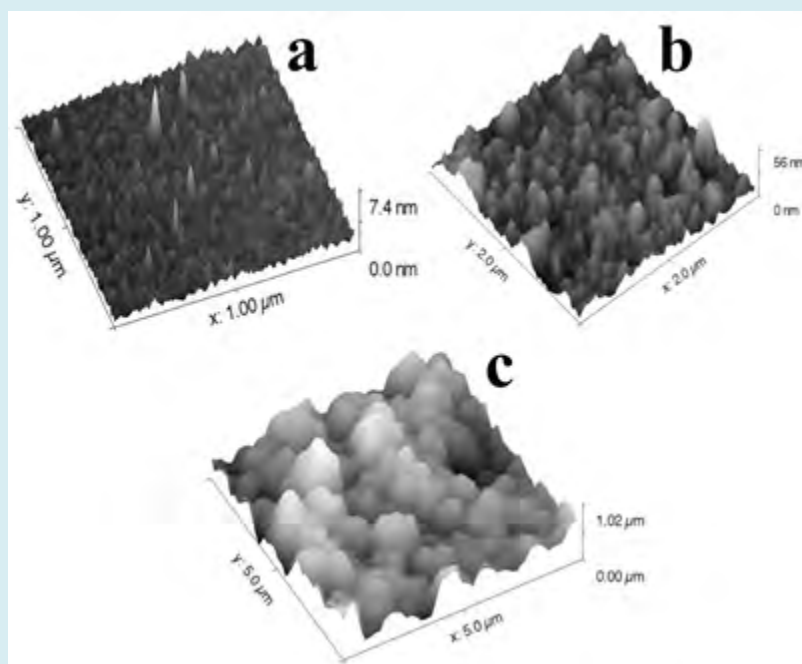


Figure 2: AFM images of; (a) metal deposited Si/SiO₂ substrate. (b) CNT deposited surface on Ni Catalyst. (c) CNT deposited surface on Co substrate.

Catalyst	Growth temp. (°C)	Growth time (Min.)
Ni	900	10/20
Co		10/20
FeCl ₃ .6H ₂ O/ZnO	1100	10

Table 1: Sample details and CNT growth parameters for different samples.

Figure 3 shows the scanning electron micrographs (SEM) of the grown CNT with different catalysts. The temperature and time of growth found to be very important and affects the shape diameter and quantity of CNT formation. Fig. 3 shows that higher growth time ~ 20 min an excessive black layer has been found and growth time in between 10-20 min, the homogeneous formation of CNT occurs while the growth time ≤ 10 min the CNT formation didn't occur. When the CNT growth ceases due to catalyst poisoning with excess carbon that supersaturated metal-carbon assembly might crystallize in carbide, oxide or silicates because of silica

supported growth. The possibility of distortion in the lattice constant value might happen because the lattice constants vicinity of metal and their compounds as well small-size effect of formation during CNT growth. Moreover, catalyst provides stiffness and mechanical reshaping during CNT growth process that that there is feasibility of metal catalysts to be in liquid state during catalytic decomposition. However, this shape distortion occurs due to relative displacement of different atomic layers in solid state due to the large forces exerted by the surrounding CNT in the growth stage.

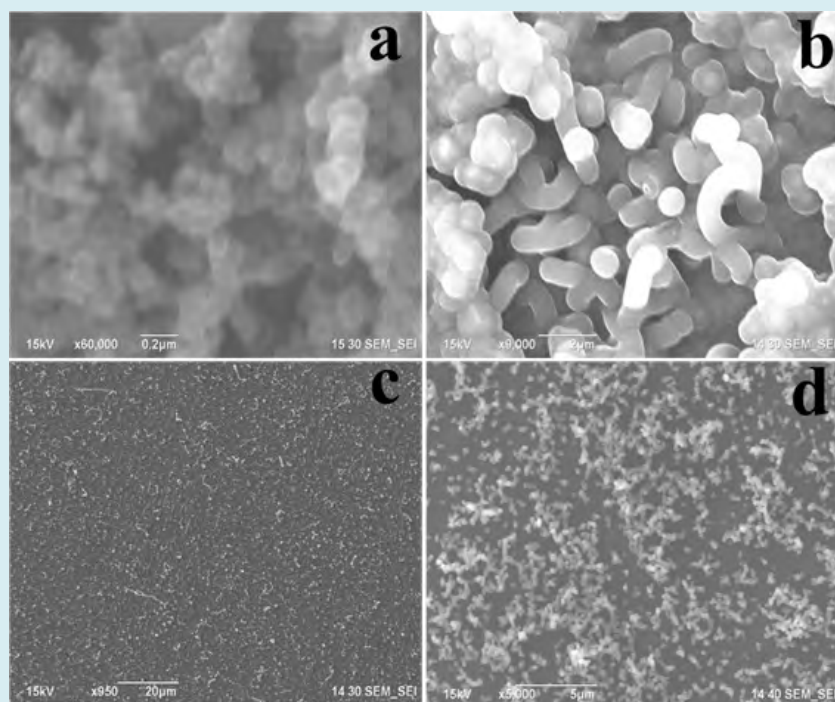


Figure 3: SEM images of grown CNT on; a) Ni catalyst at 900 °C for 20 min. b) Co catalyst at 900 °C for 20 min. c) Co catalyst at 900 °C for 10 min. d) FeCl₃.6H₂O/ZnO catalyst at 1100 °C for 10 min.

When a hydrocarbon vapor comes in contact with the hot metal-particles, first decomposes into carbon and carbon gets dissolved into the metal. After reaching the carbon-solubility limit the dissolved carbon precipitates out and crystallizes cylindrically without any enclosed bonding, which is energetically very stable. Meanwhile this decomposition process releases some heat to metal exposed zone while

crystallization absorbs some heat from precipitation zone. When the catalyst-substrate interaction is weak hydrocarbon decomposes on top surface of the metal, carbon diffuses down through the metal and CNT precipitates out across the bottom pushing the whole catalyst off the substrate called as tip-growth. In the other case, when the catalyst-substrate interaction is strong, initial hydrocarbon decomposition and

carbon diffusion take place similar to that in the tip-growth case, but the CNT precipitation fails to push the metal particle up; so the precipitation is compelled to emerge out from apex of the catalyst. Subsequently, hydrocarbon decomposition takes place on the lower peripheral surface of the catalyst and carbon diffuses upward. Thus CNT growth occurs, catalyst rooted on its base called as base-growth model. The growth of CNT has been performed with ZnO semiconductor because of its wide band gap and potential applications in optoelectronics and unique sensing behavior, which might change emission spectra and improve the crystallinity of grown hybrid nanostructure. The use of ZnO catalyst for CNT growth is applicable for sensing device applications because of its band illumination with photons. Thus, there might be the possibility of two reactions; oxidation of generated holes and electron reduction simultaneously. The degradation rate can be easily enhanced by the reduction of e-h pair recombination, which can prevent the clumping and

increased the adsorption capacity.

The above results show that the chemical reaction/diffusion between catalysts and substrates impairs the activity of the catalysts and while incorporated with carbon form a CNT-metal composites structure depending on their stability and catalytic property, many researchers mentioned [30] that all metal powders are possible to be used as catalyst carrier for CNT growth by CCVD. However, we can see clearly that the formation of the shapes like tubular, spinal, capsule or tubic structure depends on the growth temperature and precursor used.

Figure 4 shows the energy dispersive X-ray spectra and mapping of the prepared metal and semiconductor based material and their composition, which confirms the presence of deposited catalysts in the fabricated carbon structured material.

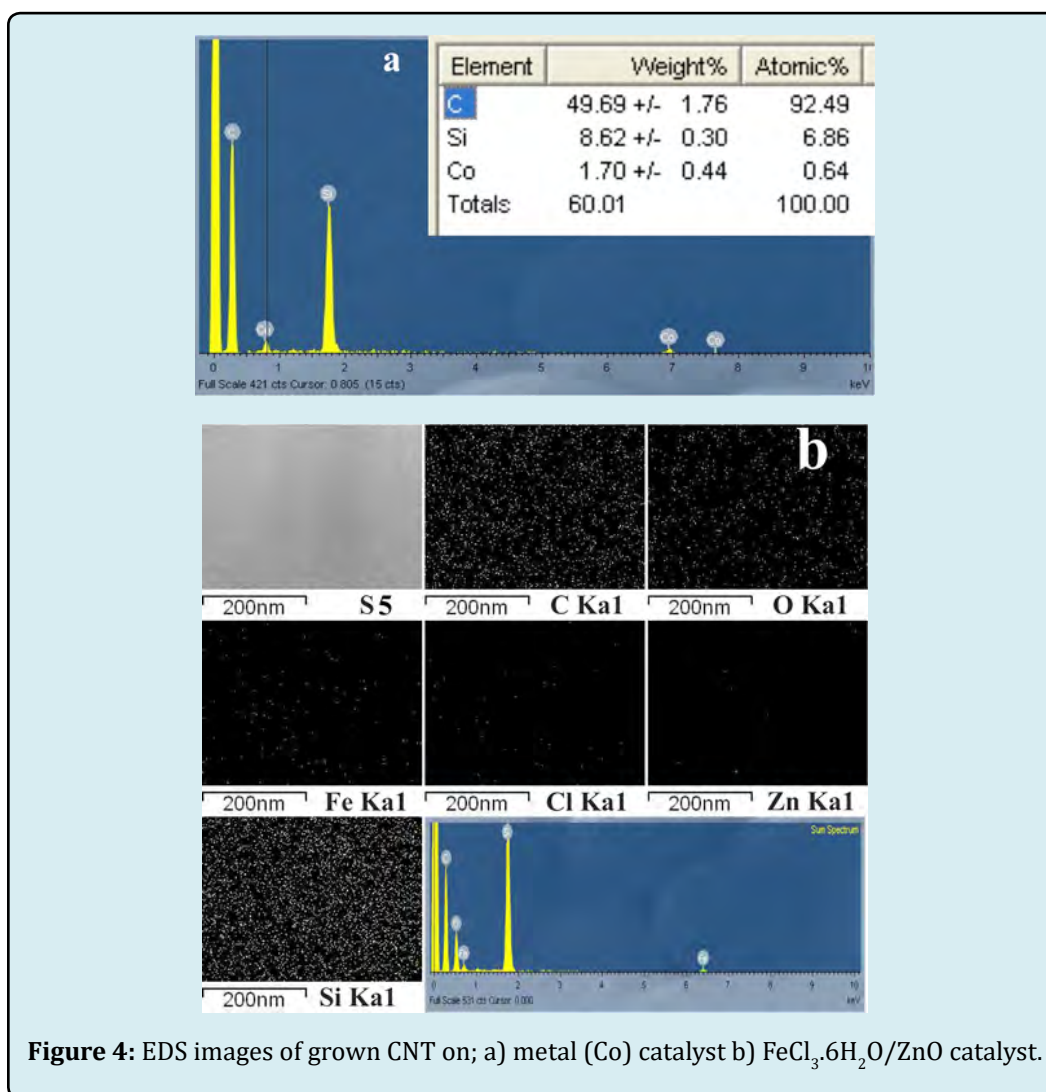


Figure 5 predicts the transmission electron microscopy (TEM) images of CVD growth of CNT on Ni, Co, Au and ZnO catalysts at different time and temperature. TEM images shows clearly the mechanism for CVD growth of CNT for Au, Ni and Co catalysts were quite different, Ni particles got accumulated on edge of grown CNT and the end shows pin shape structure covered with Ni metals while in case of Co the upper edge is open and circular. The presence of Ni

and Co catalysts on the edges and inside can also be seen by the electron diffraction pattern, which also confirmed by the “CaRIne Crystallography” software program. Fig. 5d shows the multilayers hexagonal structure, which proves the multilayered CNT growth. Formation of black layers inside the CNT is happening because the absence of H₂ gas, which increases the reaction rate for the carbon nanotube formation.

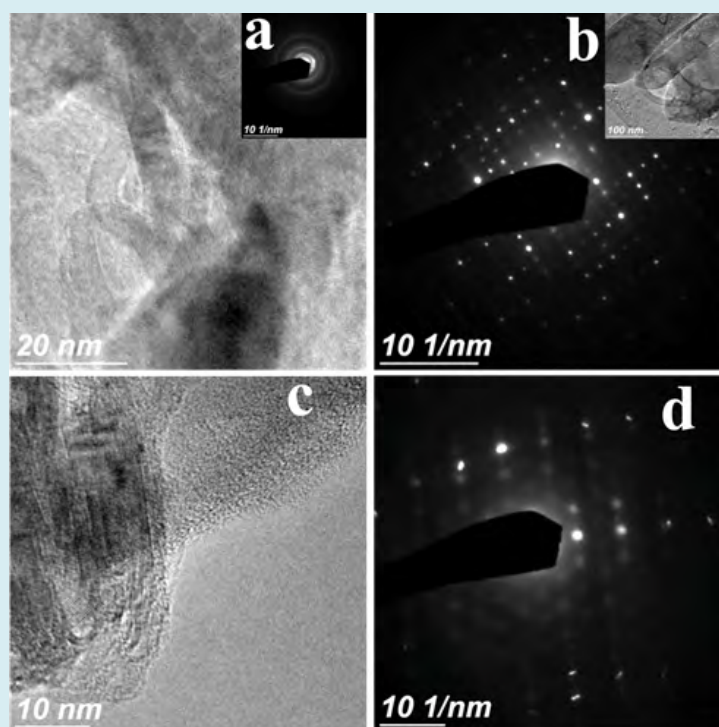


Figure 5: TEM micrographs of grown CNT at different catalysts. a) and b) represents the CNT clusters and Ni accumulation at the top edge of the Ni based grown nanostructured at 900 °C for 10 min respectively. c) and d) shows the Co based CNT grown structure and hexagonal atomic distribution of carbon atoms for 10 and 20 min growth respectively.

Figure 6 shows the Raman spectra of grown CNT using laser 532, which is also compared with the pristine MWCNT of Sigma-Aldrich using 514.5 nm laser beam. The crystalline graphite proceeds the disordered structure (D band) at ~1350 cm⁻¹ and the vibrational mode at 1585 cm⁻¹ because of the sp² orbital domain of the carbon (G Band) in case of ZnO based carbon structure growth while D band is absent in Co based growth because of the selection rule of perfect graphite structure which is forbidden. Therefore, on metal catalyst based growth the its is very hard to confine the amorphous and crystalline carbon growth. The results show the similar Raman shift and the two strongest peaks of D and

G band shows the clear formation of CNT growth on Co and ZnO based catalysts. The D band peaks observed at 1390, 1336 cm⁻¹ and G band at 1589 and 1597 cm⁻¹ for Co and ZnO based CNT growth respectively, which was in close proximity to pristine Sigma Aldrich MWCNT of 95 % purity of D and G band peaks; 1348, 1579 cm⁻¹. I_D/I_G value of grown CNT was 1.51 and 0.91 for Co and ZnO based catalytic growth. Since the disordeness of the graphite like system increases with the preparation temperature that is why the I_D/I_G values are higher in case of Co based CNT growth compared to the ZnO based also the second ordered D peaks are visible in Co based growth while not in the ZnO based CNT growth.

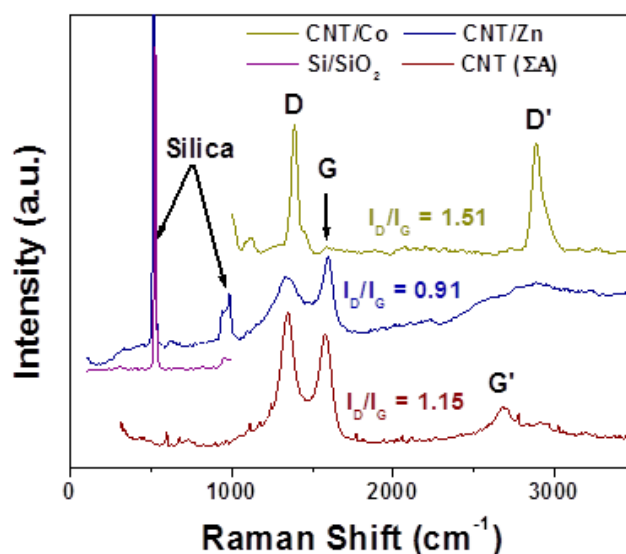


Figure 6: Raman spectroscopic measurement Co and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{ZnO}$ catalysts based CNT growth for 10 and 20 min using 532 nm laser. A comparative spectrum of silica and pristine MWCNT of Sigma-Aldrich has been shown for the confirmation of Si and CNT peaks using laser 532 and 514.5 nm respectively.

Conclusions

In this paper it was demonstrated that CNT can be grown on Si/SiO₂ substrate depositing different metal and semiconductor catalysts using acetylene as a carbon source at 900 & 1100°C temperature. The uniformity of the growth process, amount of impurity and the shape of the growth nanoparticles depend on growth time and temperature. Lower flow rate and lesser the time makes the nanocomposite growth more separated and uniform while the higher the flow rate and growth time make inhomogeneous and variability in the morphology. The thickness of the deposited catalyst particles makes a crucial role in the formation and shape of the nanostructured materials, as thinner the catalyst thickness the formation of the composite materials was helical while catalyst thickness is thick the shape is capsule/worm type structure.

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