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ORIGINAL ARTICLE

Growth of Carbon Nanotubes on Silicon Substrate and Nickel Catalyst by Thermal CVD using Ethanol

M. Ghoranneviss [1] , A.H.Javid [2] ,F. Moattar [3], A. Mashinchian Moradi [4],P.Saeedi[5]*
[1] Plasma Physics Research Center, Science and Research branch, Islamic Azad university, Tehran, Iran
[2] Department of Marine Industry , Faculty of Marine Science and Technology, Science and Research branch, Islamic Azad university, Tehran, Iran
[3,5] Department of Environmental Engineering , Faculty of the Environment and Energy, Science and Research branch, Islamic Azad university, Tehran, Iran
[4] Department of Marine Biology , Faculty of Marine Science and Technology, Science and Research branch, Islamic Azad university, Tehran, Iran
*Corresponding Author: pouneh.saeedi@srbiau.ac.ir

ABSTRACT
In this research, carbon nanotubes were grown through thermal chemical vapor deposition. Argon, ethanol vapors, and nickel deposited on silicon substrate were used as a carrier gas, carbon source, and catalyst, respectively. The experiment was performed in atmospheric pressure at 650, 750, and 850 ℃ for 15 minutes and the impact of temperature on the growth of carbon nanotubes was studied. The synthesized Nanotubes were examined by a scanning electron microscope and Raman spectroscopy.
Key words : *Carbon nanotubes, TCVD ، SEM , Raman spectroscopy*

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INTRODUCTION

Carbon nanotubes (CNTs) possess unique properties owing to their dimensions and morphology, and have been the subject of intense research efforts since their discovery. The main parameters for the growth of CNT by The chemical vapor deposition (CVD) are the hydrocarbon source, the type of catalyst and the growth temperature [1].

The CVD method uses a carbon source in the gas phase and a plasma or a resistively heated coil, to transfer the energy to the gaseous carbon molecule. Commonly used carbon sources are methane, carbon monoxide and acetylene. The energy source cracks the molecule into atomic carbon. The carbon then diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) and binds to it.

CNTs are formed in this procedure if the proper parameters are maintained. Good alignment as well as positional control on a Nano metric scale are achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes is also achieved. Use of an appropriate metal catalyst permits preferential growth of single-walled rather than multi-walled nanotubes [2].

Naveen Krishna Reddy *et al*. (2006) studied the growth of carbon nanotubes on nickel surface and the impact of surface roughness on the formation of carbon nanotubes, and showed that these nanotubes are directly influenced by surface roughness such that reducing of surface roughness can decrease the density of carbon nanotubes and increase the number of formation zones[1].Various metals and mixtures were applied by Alberto Ansaldo *et al*. [3] as catalysts for growing carbon nanotubes on silicon substrates by thermal chemical vapor deposition (TCVD). Their results showed that pure cobalt and pure nickel were more efficient that iron and molybdenum, and a mixture of nickel and cobalt were more efficient on growth at low temperatures [3].

In another study, the growth of carbon nanotubes was directly studied on nickel substrates through TCVD at different temperatures and the effect of temperature was examined on the growth of carbon nanotubes [4].

In a similar study, carbon nanotubes were grown on nickel substrates via TCVD method; propylene was used for nanotube growth in the process. Various methods have been used to prepare samples with Ni substrates.X-ray diffraction studies showed relatively homogeneous layers of carbon nanotubes growing at 700 and 800 °C [5].The present paper studies the synthesis and growth of carbon nanotubes on silicon substrates at 650, 750, and 850 °C for 15 minutes through TCVD, using nickel as the catalyst.

MATERIALS AND METHODS

Catalysts such as iron, cobalt, and nickel, which are deposited on the substrate before growth, are required for the growth of carbon nanotubes. In this test, nickel was deposited on a silicon substrate through direct current (DC) plasma sputtering.

Preparation of substrates

In this study, silicon was chosen as the substrate due to the high growth temperature and the possibility of substrate melting.First, the silicon substrate was cut in 1×1 cm^2 pieces and then placed in a beaker containing acetone in an ultrasonic bath for 15 min to eliminate any surface contamination of the samples including fats.Then the first step was repeated but in ethanol rather than acetone. Finally, the substrates were removed from the beaker using forceps and dried at room temperature.

Nickel deposition

CNTs growth requires a thin layer of a few nanometers of a metal catalyst to be deposited on the substrate before growth.In this study, nickel was used as a catalyst. Nickel was deposited on the substrate using DC plasma sputtering method .

Some substrates prepared in the previous step were put by a forceps on a steel plate already cleaned by sanding and acetone. Nickel base was used for deposition of Ni. The device was first vacuumed by a pump to a pressure of 10^{-2} Torr. In the vacuum environment, at voltage of 1 Kv, current of 160 mA, and pressure of 5.1×10^{-1} Torr for 30 min, the argon gas was converted to plasma through creating a potential difference. The plasma hit and hence detached nickel particles from its base and shed them on the silicone substrate.After the deposition, argon was stopped and the samples were removed after normalization of the pressure and cooling of the system. To ensure nickel deposition on the silicon substrate, XRD images were prepared, which are shown in (Figure1).

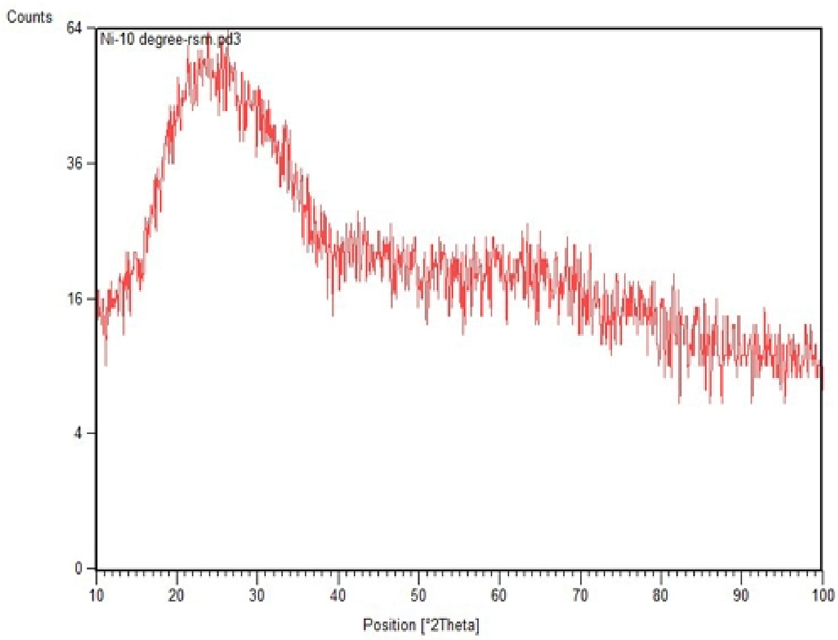

Figure1 : XRD results of Ni catalyst

Synthesis of carbon nanotube

At this stage, the TCVD system model ATU(10-30)S in the Research Center of Plasma Physics, Science and Research Branch, was used to grow carbon nanotubes on the substrates made in the previous step. This device consists of a horizontal open-ended furnace, a quartz tube with a length of 800 mm, a diameter of 75 mm, and a designed temperature of 1100 ^{0}C, which is connected to a computer to digitally adjust the temperature and time. In this study, argon and ethanol were used as the carrier gas and the carbon source, respectively.

The gas was supplied by two capsules; the first was connected directly to the furnace input and the second to a tank full of liquid ethanol. The ethanol container was placed in a water container on a heater to produce ethanol vapor.After putting the ceramic container in the center of the tube, the furnace was turned on and adjusted at atmospheric pressure, at temperatures of 650, 750, and 850 °C.

Two pieces of nickel-coated silicon substrate were placed in the furnace in a ceramic boat and in the center of the quartz tube. Before the synthesis of nanotubes, the quartz chamber was first filled with argon to prevent reaction and contamination of the substrate with the environmental gases during heating.The reduction operation was performed to achieve the desired temperature for 100 minutes under argon gas flow rate of 200 sccm.

After the reduction step and achieving the desired temperature, the first capsule valve was closed and the second capsule attached to the ethanol container was opened; this led to the entrance of ethanol vapor into the furnace while passing of argon with an argon gas flow rate of 200 sccm.

Argon flow and ethanol vapor were allowed to enter the reactor for 15 min, during which the extra ethanol and argon were driven out of the system through the pipe's outlet. After a specified period of time, the furnace was turned off automatically and carbon source was disconnected (the second cylinder valve was closed) and argon was flowed into the tube (the first capsule valve was reopened) until the furnace was cooled and reached to room temperature. During cooling of the furnace, only argon with a flow rate of 200 sccm was entered and the samples were removed after cooling from the furnace. Figure 2 show the schematic picture of the steps.

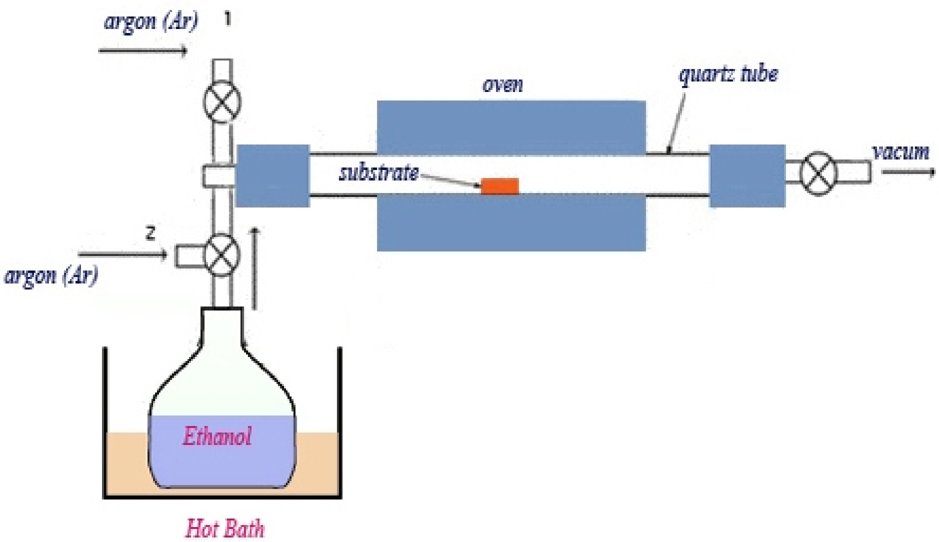

Figure 2 : Schematic diagram of the TCVD experimental apparatus

Characterization

Raman spectroscopy is a complete method for recognizing the characteristics of single-wall and multi-wall CNTs.After completion of the growth steps in the furnace, Raman spectroscopy was used to detect the nanostructures. Raman spectrometer, Thermo Nicolet Dispersive used in this study had a laser wavelength of 532 nm, spectroscopic range of 100-4200 cm^{-1}, and precision of 4 cm^{-1}. Raman spectrum of the CNTs grown on Ni catalyst at 650,750 and 850 ^{0}C, for 15 min are shown in (Figure 3).

The most common instrument used to evaluate the quality of the carbon nanotubes is the scanning electron microscope (SEM) whose images provide useful information about the formation of carbon nanotubes, the products relative purity, and their diameter distribution [6].The obtained samples were photographed and analyzed using a scanning electron microscope, FE-SEM, model S-4160, made by Hitachi Co, Japan, with a voltage of 20 and 30 kV.

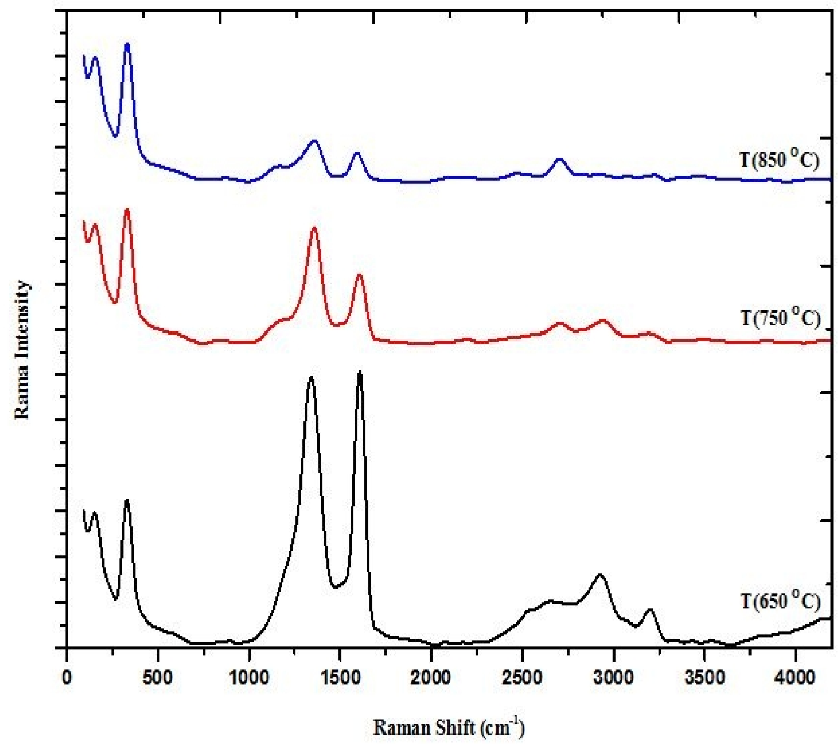

Figure 3 : Raman spectrum of the CNTs grown on Ni catalyst at 650,750 and 850 ^{0}C, for 15 min

RESULTS AND DISCUSSION

As can be observed in Figures, there are three peaks in the Raman spectrum. In general, the Raman peaks between 1550 and 1600 cm^{-1} (usually 1590) are known as the peaks of band G or G-band and are related to the graphitic properties of nanotubes. Peaks between 1300 and 1360 cm^{-1} (usually 1350) are known as the peaks of band D or D-band and indicate a defect in the graphite structure or the presence of amorphous carbon. A low frequency peak (less than 200) called the radial breathing mode shows the radial breathing mode of carbon nanotubes by which their diameter can be realized. This peak is not seen in the spectrum of graphite and is the main character of single-wall carbon nanotubes. In most cases, the quality of the sample is evaluated by the ratio of G-band to D-band intensity. A higher ratio indicates a lower level of amorphous carbon.

D- band to G-band intensity ratio is a determining parameter in the purity of the samples; $I_D<I_G$ represents high purity of the graphite structure of carbon and high quality of nanotubes and $I_D>I_G$ reflects high impurity of the produced nanotubes [7]. As shown in Table 1, I_D was smaller than I_G at 650 °C. Figure 4 depicts the CNTs growth on the silicon substrate and nickel catalyst at different temperatures.As can be seen in the Figures, the tubes have varying diameters. Moreover, the nickel particles on the opening of the nanotubes indicate that the growth is as “tip-growth mechanism” [8].

In this type of growth, the carbon derived from absorption and degradation of methane over the upper surface of nickel nanoparticle, is diffused around or in its middle and deposits in the lower part of catalyst nanoparticle to form the nanos. In Figure 5, a schema of this type of growth is shown [9].

Table 1 : Ratio between the intensity of G and D peaks at different temperatures

Catalyst	T(^{0}C)	I_D/I_G
Ni	650	$I_D<I_G$
	750	$I_D>I_G$
	850	$I_D>I_G$

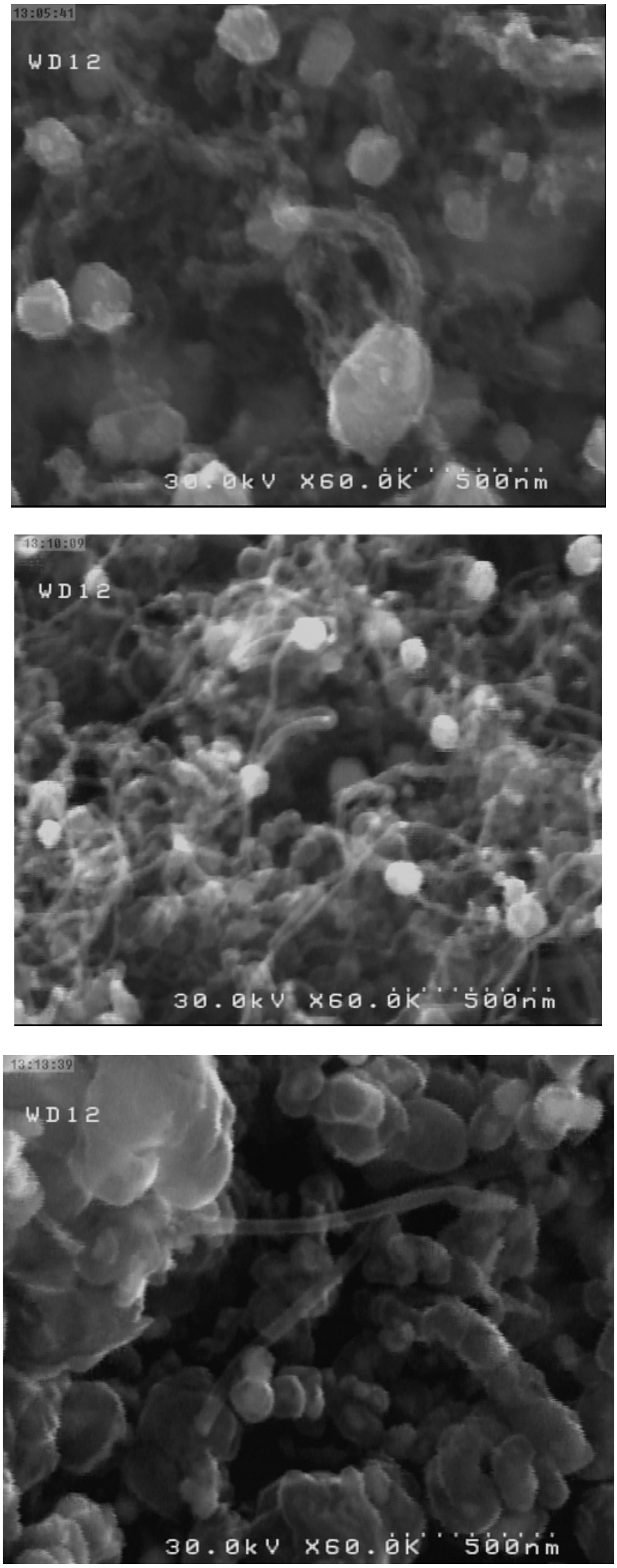

Figure 4: The SEM images of CNTs grown over Nickel nanoparticles distributed on the silicon substrate by thermal CVD,(a) at 650^{0}C,(b) at 750^{0}C and(c) at 850^{0}C for 15 min

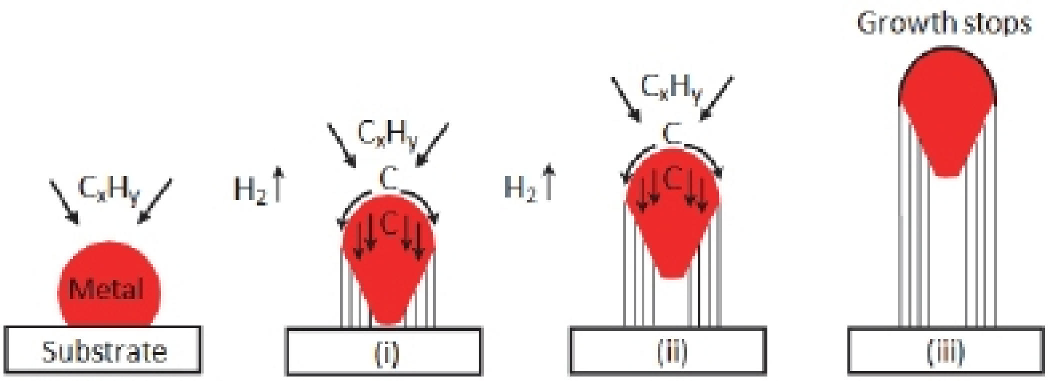

Figure 5: tip-growth mechanism of the carbon nanotube [9]

CONCLUSION

In this paper, the growth of carbon nanotubes on silicon substrate using the TCVD system and nickel catalyst was studied in atmospheric pressure at 650, 750, and 850 °C for 15 minutes. SEM and Raman spectroscopy analysis showed that the temperature is an effective parameter for nanotube growth.The grown nanotubes were multi-walled and had high quality at 650 °C, according to the ratio of I_D/I_G. As the temperature increased to 850 °C, better nanotubes were produced.

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