EFFECT OF GAS FLOW RATE AND GAS PRESSURE ON THE CARBON NANOTUBES PREPARED BY MPECVD

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In this work we present our results about the preparation of carbon nanotube with different morphologies by using microwave plasma enhanced chemical vapor deposition MPECVD. Well aligned, curly and coiled carbon nanotubes have been prepared. We have investigated the effect of the different growth condition parameters such as type of the catalyst, pressure and the hydrogen to methane flow rate ratio on the morphology of the carbon nanotubes. The results were showed that there is a great dependence of the morphology of carbon nanotubes on these parameters. There is a linear relation between the growth rate and the methane to hydrogen ratio. The effect of the gas pressure on the CNTs was also studied. Our samples were investigated by scanning electron microscope, Raman spectroscopy.

Introduction

No one can deny that since the discovery of fullerrenes in 1985[1] and then the carbon nanotube in 1991[2] there is a very intensive work on the world nanoscince and nanotechnology. Off course this due to the very useful applications of these materials in many fields. Especially carbon nanotube has been received a great attention because of their unusual electrical mechanical and optical properties. There are many methods for the production of carbon nanotube. Between them it is possible to produce nanotubes with differing properties and in different forms. The most common methods used for the production of nanotubes are arc discharge [3], laser vaporization [4], and chemical vapor deposition (CVD). Our interest lies mainly in the area of electronic device applications, for which CVD is particularly suitable as it allows the location of nanotubes to be precisely controlled. PECVD is relatively a new technique. Depending on the way of the plasma generation there are many types of PECVD such as D.C., radiofrequency and microwave. Microwave plasma-enhanced chemical vapor deposition (MPECVD) method has been regarded as one of the most promising candidates for the synthesis of CNTs due to the vertical alignment, the large area growth, the lower growth temperature, uniform heat distribution and the good control of the different growth parameters.

In the literatures there are a lot of reports about the preparation of CNT by using MPECVD. Recently, Fang et al. showed the effect of using Fe catalyst in the elemental and oxidized forms. The researchers showed that the using of oxidized catalyst providing well-dispersed Fe nanoparticles for the growth of uniform CNTs by preventing the reaction of Fe catalysts with the Ti-buffer layer[5]. In reference [6] a comparative study between radiofrequency (RF) and pulsed-DC plasma sources for PECVD of CNTs was described. Pulsed-DC plasma has higher power density and electronic temperature inducing a higher ion density and enhancing ion bombardment on the substrate. In this paper we present our results about the preparation of CNTs with different morphology. The effect of methane to hydrogen ratio, pressure on the formation of CNTs is investigated by using SEM and Raman spectroscopy. CNTs with different morphology such as well aligned, curly, regular coiled and carbon nanosphere have been prepared by using MPECVD.

Experimental Work

n-type Silicon (100) wafers ,with oxide layer (SiO_2) with thickness ~ 80 nm. The resistivity of silicon wafers was 500 Ω cm, were cleaned ultrasonically by acetone for 20 min. at the room temperature and then washed many times by distilled water. Then the cleaned samples were introduced in to the magnetron sputtering to make a catalyst layer. In this study we have used cobalt and nickel with different thickness as catalyst in order to activate the growth of carbon nanotube.

The magnetron sputtering was initially evacuated to about $1x10^{-5}$ torr base pressure. Argon gas was introduced until the pressure reaches 10 millitorr. The power of argon plasma was 30 watt. The substrate was at room temperature during the deposition process.
CNT synthesis was grown by using SEKI AX5200S microwave PECVD reactor. The heating of the substrate was supplied by 3.5 kW radio frequency power supply. The substrate surface temperature was measured by using a Williamson (model 90) dual wavelength.

The silicon samples with catalyst were introduced into the MPECVD reactor, which was then evacuated to about 1 $x10^{-6}$ Torr by an external mechanical pump. After reaching to this base pressure, the high purity hydrogen gas (99.9999) was opened in order to reduce the sample and in the same time the heater was switched ON to the selected temperature. In order to make nano island catalyst, the samples were subjected to the pretreatment process. The pretreatment was made at temperature 650 ^{0}C. Plasma power was 500 watt, H_2 flow rate was 80 sccm and the time of pretreatment process was 3 minutes. After the end of the H_2 plasma pretreatment, the high purity methane gas (99.9999) was opened for five minutes before the plasma switched on and that in order to insure that methane flow is steady. The growth conditions were fixed as fellow plasma power 500 watt and gas pressure 16 torr (~2.13 kPa). H_2 flow rate 80 sccm (standard cubic centimeter per minute) and methane 20 sccm and the growth time was 5 minutes and the growth temperature was 650 ºC. The surface morphology of the grown CNTs was investigated with the analytical scanning electron microscope JEOL JSM-6490LA with resolution (3 nm) and maximum operating potential 30 kV and the energy dispersive x-ray analysis (EDX) which is attached to the electron microscope. Raman spectroscopy was performed on the surfaces of the carbon deposits to characterize the diameter distributions of the smaller CNTs and their graphitic ordering by using (NT-MDT, NTEGRA Spectra) with excitation Ar laser 473 nm at room temperature.

Results and Discussions

Scanning electron microscope characterization

The typical SEM images of the grown CNTs film are shown in Fig. 1. Indicating that the nanotubes are about 40–100 nm in diameter and well beyond several tens of micrometer in length. It is clearly seen that the grown CNTs contain some amount of carbonaceous particles adhering to the walls of nanotubes when using a small amount of methane as shown in Fig. 1 (k) also from the cross-sectional SEM image of the CNTs films we have noticed that the nanotubes are randomly distributed on the substrate and misaligned except fig. 1a where the CNTs are highly aligned. We found that the growth rate has a great dependence on the amount of methane. For example the growth rate varied from 1.34 μm/min when the methane flow rate was 10 sccm to more than 14 μm/min when the methane flow rate was raised to 50 sccm. This growth rate is greater than that reported in the literature [6]. The relation between the growth rate and methane to hydrogen ratio is shown in fig. 2. It is clear that as the flow rate of methane gas increases the amount of carbon in the growth area also increases and the growth rate in turn will be increases [6]. It was very interesting to see the carbon nanosheet formed at different locations of the carbon nanotube. For example figure 2 shows the formation of carbon nanosheet at the end and at the middle of the carbon nanotube. It was very interesting also that when we want to see image under SEM the carbon nanosheet moved down to the substrate side under the effect of the electron beam. Figure 4 shows the carbon nanotube with different morphology. In fig. 4a we can see the formation of the carbon nanocoil with diameter 120 nm and several micrometers in length. The shape of this nanocoil is differs from that in the previous work. Here the carbon nanocoil is a fish-bone like and it may be formed due to the anisotropic property of the catalyst particle at the top.

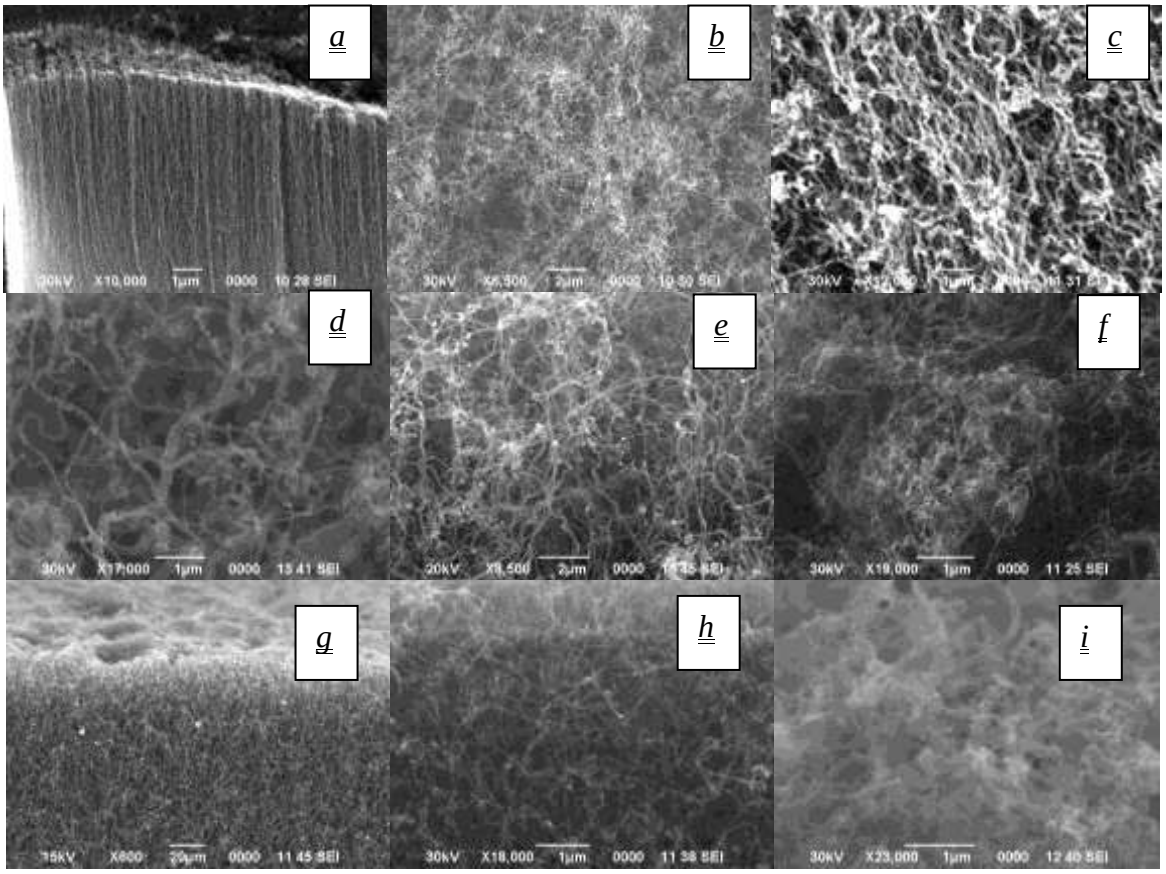

Fig. 1. Carbon nanotubes prepared by using different cobalt thickness and different methane portions.(a,d,gand i)represents the CNTs grown at 10,20,40and 50 sccm methane flow rate respectively, by using Co of thickness120 nm and (b,e and h) for thickness of 6o nm and(c,f) for thickness of 30nm

It well known that when the catalyst particle is big at the gas side and relatively small at the substrate side, carbon atoms will be precipitated to form this shape (fish-bone) [7]. The catalyst particle has been observed at the top of the grown carbon nanotube, which indicating that the CNTs are grown by the tip mechanism. The carbon nanosphere (or CNS) has been noticed during the SEM investigations as shown in figure 4c.the analysis with the EDX showed that this sphere is consisted from carbon.

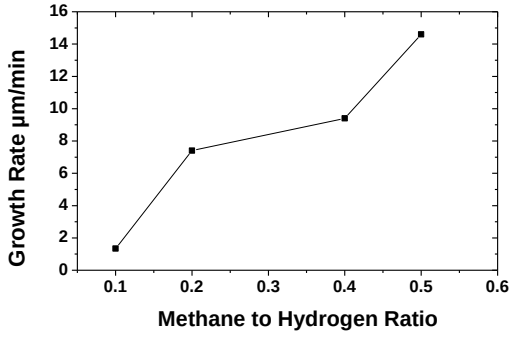

Fig. 2. Effect of the ratio between methane and hydrogen on the growth rate of CNTs

These CNS were observed with relatively small amount and distributed over the curly CNTs. Although the diameter of this sphere was about 3.29 μm, other spheres with smaller diameter were also observed during the SEM investigations. The majority of CNTs that we have prepared are curly or irregular coiled carbon nanotube as in fig. 4b, c.

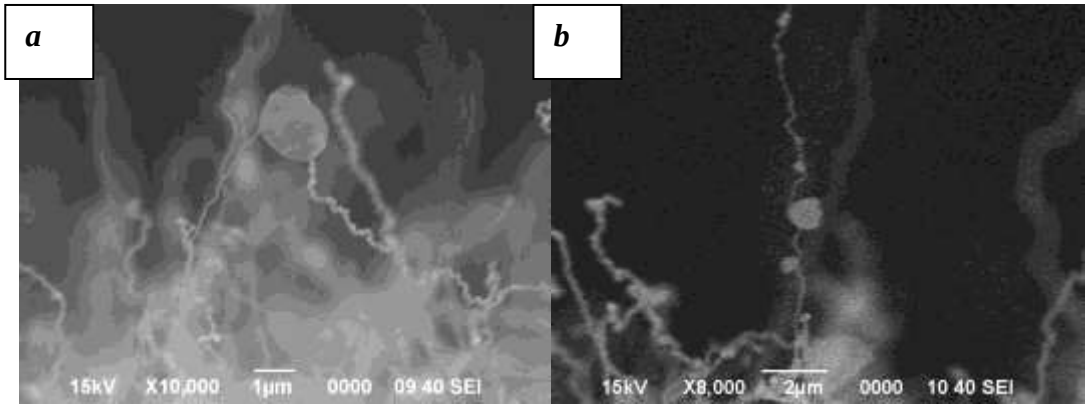

Fig. 3. Formation of the carbon nanosheet at the end of CNTs(a), and at the middle of CNTs(b)

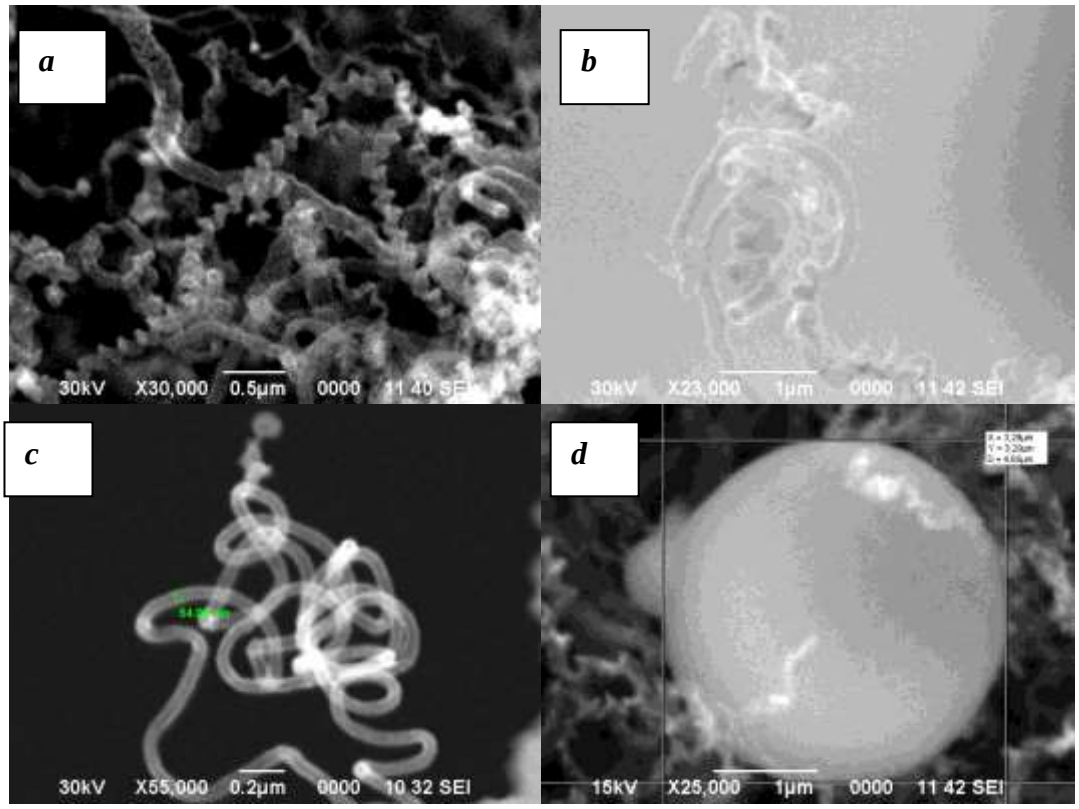

Fig. 4. Carbon nanotube with different morphology

In order to develop advanced engineering materials with excellent mechanical properties, CNTs are used as a good reinforcing phase for structural composites, such as polymers, metal, and ceramics. Compared with conventional CNTs, the coiled CNTs can provide a much larger contact area to the

matrix, which can provide a much larger interfacial strength and thus improve mechanical properties. Consequently, the CNTs with special structure can furthermore improve the mechanical properties of the composites [8].

Raman spectroscopy

Raman spectra have been measured to investigate the crystal quality and structure of CNTs. Fig. 5 shows the Raman spectra of CNTs which were grown on the Si substrates by using cobalt as a catalyst with thickness of about 120 nm in different methane to hydrogen ratio (20 and 50 sccm). The Raman spectra (excitation wavelength 473 nm) of all samples show D-band peak at around 1300 cm^{-1} and G-band peak at around 1580 cm^{-1}, which indicate that our CNTs are multi wall CNTs (MWCNTs) [9]. The D-band and the G-band correspond to sp^2 and sp^3 carbon stretching modes relatively, and their intensity ratio is a measure of the amount of disorder in the CNTs. The D-band is known to be attributed to the carbonaceous particles, defects in the curved graphitic sheet and tube ends [10]. Raman spectra of the sample in figure (1a) are represented in figure (5). There are two characteristic peaks at 1354 cm^{-1} and 1574 cm^{-1} and D-overtone band at around 2701 cm^{-1}. As one can see form the graph, the peaks are slightly shifted to the higher frequency value as the amount of methane flow rate increased, which indicating that there is a smaller stress on our CNTs.

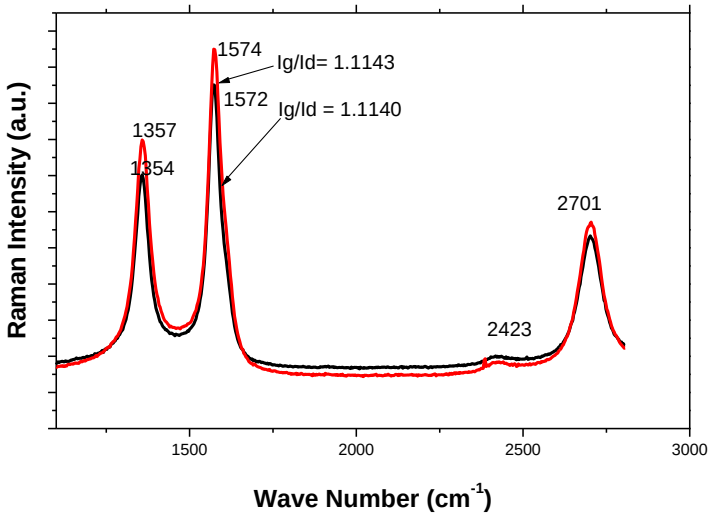

Fig.5. Raman spectrum of the carbon nanotube in figure (1a, g)

It has been suggested that lower I_g/I_d ratios and narrower first and second order D and G bands are suggestive of well-aligned CNTs [11]. Therefore, the Raman spectroscopy characterization results coincided very well with the SEM observations shown in Fig (5). Table (1) represents the variation of the ratio (I_g/I_d) with methane flow rate at different thickness. From these data one can conclude that for all thicknesses the ratio increases to maximum value and then go down again and this suggested that there is an optimum value for the methane flow rate at about 30 sccm. Effect of the methane flow rate on CNTs was also studied with nickel as a catalyst on silicon substrate and by using TiN as a buffer layer. The same effect was also observed. Figure (8) illustrate the Raman spectrum of CNTs grown on Ni/TiN/Si substrate. A shift of about 10 cm^{-1} was observed when the methane flow rate varies from 10 sccm to 50 sccm which indicating that there is a smaller stress as the amount of methane is increased by adding more carbon layers to the CNTs as because the CNTs suffers a tensile residual stress in comparison with that in nanosheets because the latter consists of grapheme planes without bending stress [12].

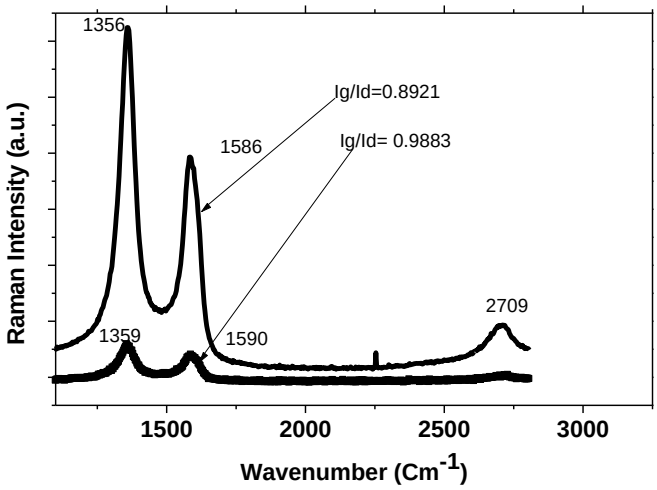

Fig.6. Raman spectrum of the carbon nanotube in figure (1b, h)

We note the appearance of the radial breathing mode RBM, as shown in the inserted graph in figure (7). There are three intensive peaks at 18.3 cm^{-1}, 309 cm^{-1} and 412 cm^{-1} for the sample with methane flow rate equal to 50 sccm and two peaks at 18.3 cm^{-1} and 412 cm^{-1} for the sample with methane flow rate equal to 10 sccm .At a first-order approximation, if the relationship between the SWCNT diameter D and Raman shift ω, D (nm) = 248/ ω (cm^{-1}) [13], is applied, and then the numerical majority of SWCNTs are found to have a diameter about 0.9 nm,0.6 nm and 13.5 nm . The effect of the gas pressure on the CNTs was also investigated. Figure (8) represents the Raman spectrum of the CNTs at different gas pressure. One can note the gradual increases in the Raman intensity for all peaks which indicates the enhancement of the CNTs quality and amount with the gas pressure increasing. When the gas pressure is low, the growth rate of the CNTs was also low because the a lot amount of carbon atoms at lower pressure may fly for long time and does not deposited at the substrate.

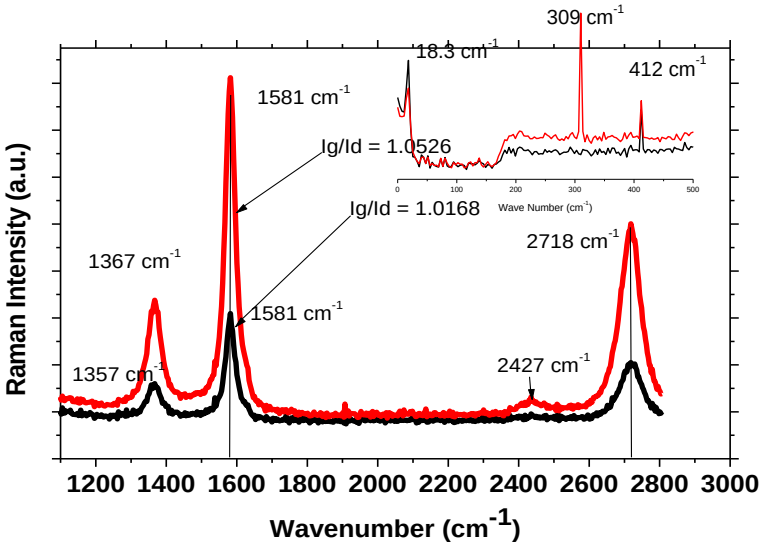

Fig.7. Raman spectrum for CNTs grown on silicon substrate using nickel as a catalyst and TiN as a buffer layer. In set the radial breathing mode (RBM)

Table 1. Ig/Id variation with methane flow rate at different catalyst's thicknesses.

CH_4(sccm)	30 (nm)	60 (nm)	120 (nm)
10	0.8921	0.9883	1.0715
20	0.9950	0.9980	1.1140
40	0.9960	0.9965	1.1143
50	0.8903	0.9889	1.0724

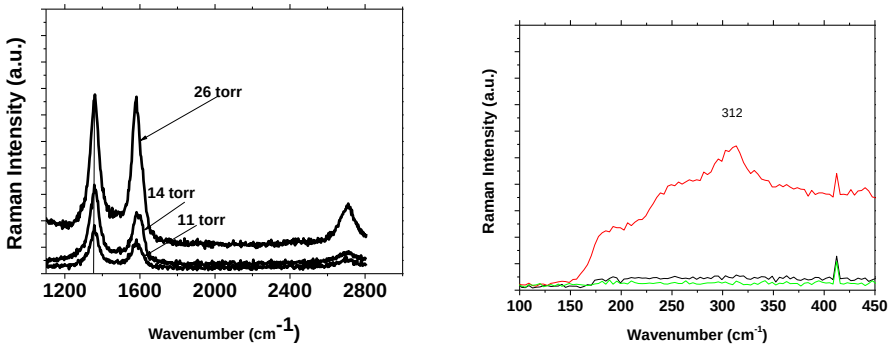

Fig.8. Effect of the gas pressure on the carbon nanotubes.

Photoluminescence measurements

With respect to the photoluminescence measurements, The PL measurements were performed at room temperature under the excitation laser with wavelength of 325 nm. The laser beam was focused onto the sample a very small spot size (of about 1mm in diameter), and this in order to avoid local oxidation of the sample. The photoluminescence spectrum of the carbon nanotubes at different growth temperature is represented in the figure (9). There are two intensive peaks near the ultraviolet range (411 nm, 433 nm for the sample at growth temperature 600 ºC). the sample at growth temperature 600 ºC represents the optimum sample for the PL among the other samples. It was observed the peaks positions shits to the higher wavelengths value as the growth temperature increases. According to the reference [14] is due to the (3, 3) single wall carbon nanotubes. Through the experiments it was observed that the photoluminescence intensity is very sensitive to the change in the angle. For example, the samples of vertically carbon nanotubes gives the maximum PL intensity at a very small angle with respect to the laser beam and the intensity gradually decreased as the angle increased, on the other hand, the samples with the horizontal carbon nanotubes gives the maximum PL intensity when the sample approximately parallel to the laser beam. This strong polarization dependence may be due to the quantum confinement effect through the diameter of the carbon nanotube. The effect of the annealing temperature on the photoluminescence was also studied. The experiments showed that the photoluminescence is completely disappeared after the annealing at 600ºC in air for five minutes.

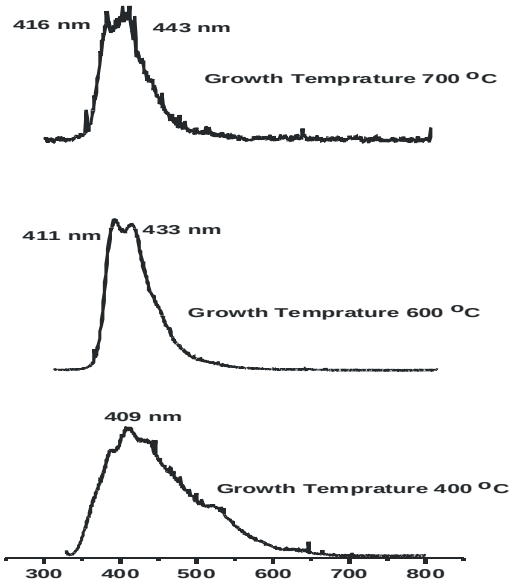

Fig.9. Photoluminescence of carbon nanotubes at different growth temperatures

It is well known that the growth of CNTs using MPECVD involves two steps; the first step is the H_2 plasma treatment in order to convert the catalyst film into nanoislands and this considered to be the most important step in CNTs growth as the diameter of the catalyst nanoparticles determines the diameter of the CNT. The second step consists of the growth of CNTs using a mixture of H_2 and a carbon source gas (CH_4 in our case). Most of the existing models for MPECVD growth of nanotubes are based on the model proposed by Baker et al. [15]. At high temperature, the decomposition of CH_4 at the surfaces of the catalytic nanoparticles (Co in our case) occurs. The carbon atoms accumulate on their surfaces and diffuse into the catalyst particles. When the accumulation of carbon atoms becomes supersaturated, a thin graphitic layer quickly encloses the catalyst particles. As the precipitation of graphitic layer continues, the CNTs are formed. Depending on the attraction force between the catalytic nanoparticles and the substrate, the growth mechanism involves the base (or root) growth and the tip growth. In the base growth mechanism, the catalytic particles stay on the substrates during the growth. In contrast, in the tip growth mechanism, the catalytic particles are detached from the substrate and located at the tip of CNTs. The growth of CTNs using MPECVD is considered to be a very complicated process because it involves many determining factors in growth conditions. The most important factors involve the catalytic material, the catalytic support material (namely, catalyst–substrate interactions), the growth temperature gradient across the catalytic particle and the effect of plasma. In addition, the effects of plasma treatment on the growth mechanism are also very effective. Although effects of hydrogen plasma on the growth of nanotubes are a very complicated process, it involves the following effects. At the first, the geometry of CNT's tip is an important factor. Their tip structure may be changed during the treatment. Secondly, the partial rehybridization of sp^2 components into sp^3 can occur during the treatment, meaning the decrease of the average work function [16]. Third, the dangling bonds on the surface of CNTs can be chemically terminated by atomic hydrogen and formed C–H bonds with low work function [17]. During the H_2 plasma treatment, the C–C bonds can be broken to form a lot of defects and the nanonodes. Ion bombardment can heat the catalytic particles to increase the diffusivity and solubility of carbon atom [18], which can result in the growth of CNTs at a relatively low temperature. According to the measurement and analysis above, it can be concluded that the growth mechanism of CNTs using Co as catalyst by MPECVD is as follow: At the first stage, the continuous Co film is transformed into the nanoparticles in form of a spherical shape under

hydrogen plasma treatment. After CH_4 is introduced into the chamber, the decomposition of CH_4 will be results in the accumulation of carbon atoms on the surfaces of Co nanoparticles. Moreover, the plasma formed above the substrate enhances the diffusion of carbon atoms into Co particles due to ion bombardment to the catalytic particles. When the diffusion of carbon atoms into Co particles reaches the equilibrium and even supersaturates, they precipitate on the surfaces of the nanoparticles. Co can dissolve a nongraphitic form of carbon and precipitate carbon as graphite as a consequence of supersaturation. The accumulation of carbon atoms is enough to form a thin graphitic layer and quickly enclose the Co particles, and this leading to the growth of cylindrical graphitic shells to form the CNTs. For the different gas ratio, the plasma intensity and the content of the provided carbon atom vary greatly. Under the appropriate content of carbon atom, the equilibrium is reached between the provided carbon atoms and the growth of CNTs, which can grow the CNTs without crystalline defects. Under the high carbon content, the provided carbon atoms greatly diffuse into the nanoparticles, leading to the result that some nanoparticles are detached from the substrate under the plasma treatment and the CNTs grow by the tip

Conclusion

CNTs with different morphology (such as well aligned, irregular coiled and regular coiled) CNTs have been successively prepared by using microwave plasma enhancing chemical vapor deposition (MPECVD).The effect of the methane to hydrogen ratio on the morphology and the structure of the CNTs has been studied by using SEM and Raman spectroscopy. The ratio of the g-band to d-band has been affected by methane to hydrogen ratio. There is an optimum value of methane to hydrogen ratio at which we can obtain CNTs with good structure and less carbonaceous particles. There is a linear relation between the growth rate the methane to hydrogen ratio. The photoluminescence measurements at the room temperature showed very narrow intensive overlapping peaks near the ultraviolet range at energy of about 3eV.

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MPECVD ӘДІСІМЕН АЛЫНҒАН КНТ-ке ГАЗ АҒЫНЫНЫҢ ЖЫЛДАМДЫҒЫ МЕН ҚЫСЫМНЫҢ ӘСЕРІ

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Берілген жұмыста бу фазасынан микротолқынды плазмохимиялық әдіс (MPECVD) арқылы әр түрлі формологиясы бар көміртек нанотүтіктерін алу бойынша нәтижелер келтірілген. Шырмалған, спираль тәріздес, жоғары ориентацияланған көміртекті нанотүтіктер алынды. Біз көміртек нанотүтіктерінің морфологиясына әсер ететін өсіру шарттарының, катализатор, қысым, сутегі ағынының метанға деген қатынасы сияқты әр түрлі параметрлерді зерттедік. Келтірілген нәтижелерге сүйене отырып, көміртекті нанотүтіктердің морфологиясының жоғарыда аталып кеткен параметрлеріне айтарлықтай тәуелді екені көрсетілді. Өсіру жылдамдығы мен метанның сутекке деген қатынасы арасындағы сызықты қатынастар анықталды. Сонымен қатар, қысымның көміртек нанотүтіктеріне әсері зерттелді. Біздің үлгілер сканирлеуші электронды микроскопта және Раман-спектроскопия қондырғысында зерттелген болатын.

ВЛИЯНИЕ СКОРОСТИ ГАЗОВОГО ПОТОКА И ДАВЛЕНИЯ НА УНТ, ПОЛУЧЕННЫХ МЕТОДОМ MPECVD

Эл-Шазли М.А., З.А. Мансуров, С.Ж. Токмолдин, Т. Айтмукан, В. Глазман, А. Никитин

В этой работе представлены наши результаты по получению углеродных нанотрубок разных морфологий с использованием микроволнового плазмохимического осаждения из паровой фазы (MPECVD). Были получены высокоориентированные, вьющиеся, спиралевидные углеродные нанотрубки. Мы исследовали воздействие различных параметров условий роста такие как: вид катализатора, давление и отношение потоков водорода к метану – на морфологию углеродных нанотрубок. Из представляемых результатов ясно видна значительная зависимость морфологии углеродных нанотрубок от вышеперечисленных параметров. Обнаружено линейное отношение между скоростью роста и отношением метана к водороду. Также было изучено влияние давления газа на углеродные нанотрубки. Наши образцы были исследованы на сканирующем электронном микроскопе и на установке Раман-спектроскопии.