ARTICLE IN PRESS

Vacuum xxx (2009) 1–5

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Growth of carbon nanotubes on diatomite

El-Shazly M. Duraia [a,b,c,*], M. Burkitbaev [b], H. Mohamedbakr [b], Z. Mansurov [b], S. Tokmolden [c], Gary W. Beall [d]

[a] *Suez Canal University, Faculty of Science, Physics Department, Ismailia, Egypt*
[b] *Al-Farabi Kazakh National University, Almaty, Kazakhstan*
[c] *Institute of Physics and Technology, 11 Ibragimov Street, 050032 Almaty, Kazakhstan*
[d] *Texas State University-San Marcos, Department of Chemistry and Biochemistry, 601 University Dr., San Marcos, TX 78666, USA*

ARTICLE INFO

Article history:
Received 2 September 2009
Accepted 28 September 2009

Keywords:
CNTs
Diatomite
Photoluminescence
MPECVD

ABSTRACT

We report the formation of vertical carbon nanotubes utilizing diatomite as a substrate. This new material combines the advantages of carbon nanotubes and diatomite in one material. The SEM investigations showed that the average diameter of the carbon nanotubes was 60 nm and the growth was through the tip growth mechanism. Raman spectroscopy was also used for the carbon nanotubes characterization and showed two intensive peaks around 1350 cm^{-1} and 1580 cm^{-1} and several peaks at low frequency range from 100 cm^{-1} to 500 cm^{-1} which are assigned to the radial breathing mode (RBM) and used as a characteristic of single wall carbon nanotubes. The photoluminescence measurements at the room temperature showed two very narrow intensive overlapping peaks near the ultraviolet range at energy of about 3 eV. And there are two peaks with lower intensity in the infrared region at 830 nm and at 940 nm (or 1.49 eV, 1.3 eV respectively).

1. Introduction

No one can deny that since the discovery of fullerenes in 1985 [1] and then the carbon nanotube in 1991 [2] there has been a very intensive work in the world of nanoscience and nanotechnology; this, of course, is due to the very useful characteristics found in materials when manipulated at the nanoscale are creating whole new applications in many fields. Carbon nanotubes have received a great deal of attention because of their unusual electrical, mechanical and optical properties. There have been many methods for the production of carbon nanotube. Between them it is possible to produce nanotubes with differing properties (metallic or semiconducting) and in different forms (single walled or multiwalled). The most common three 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 and orientation of nanotubes to be controlled with a large degree of precision. 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 low temperature and the ability cover large growth areas. Plasma-enhanced chemical vapor deposition (PECVD) is a promising rapidly developing growth technique, due to the lower growth temperature, uniform heat distribution and the good ability to control of the different growth parameters. The different properties of CNT such as the electrical and optical properties are highly dependent on the morphology and chirality of the CNT and the control of this morphology and chirality leads to the control of these properties. Diatomite is a natural material which has many useful applications such as water purification; moreover it is very cheap material occurring in nature in large easily minable quantities of high purity.

Diatomite is the skeletal remains from diatoms composed of silica with very large surface areas. The utilization of this material as a substrate combines the advantage of both CNTs and diatomite and this of course opening a very promising potential application in the water purification in the future.

In this paper we report for the first time the synthesis of vertical CNTs on diatomite. To our knowledge, until this moment, there is no report in the literature concerning such synthesis. So for the first time the advantages of carbon nanotubes as a very cutting edge material with a wide range of applications and diatomite as a very cheap natural material in one composite material which has a promising applications, especially in water purification. The samples were investigated by the scanning electron microscope and Raman spectroscopy.

---

* Corresponding author. Al Faraby Kazakh National University, Almaty, Kazakhstan. Tel.: +7 727 386 5675; fax: +7 727 386 5378.
E-mail address: duraia_physics@yahoo.com (E.-S.M. Duraia).
URL: http://www.sci.kz

0042-207X/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2009.09.012

Please cite this article in press as: Duraia E-S, et al., Growth of carbon nanotubes on diatomite, Vacuum (2009), doi:10.1016/j.vacuum.2009.09.012

2. Experimental work

CNTs synthesis was grown by using SEKI AX5200S microwave PECVD reactor. The diatomite used in this study is obtained from (Aktyubinsk/Kazakhstan) [5], diatomite sample with catalyst was loaded into the MPECVD reactor, which was then evacuated to about 2×10^{-7} torr and the pretreatment process, was done as follow, 500 °C, pressure 16 torr, plasma power 500 watt and H_2 80 sccm (standard cubic centimeter per minute) and the time of the pretreatment was 5 min. The growth conditions were fixed as follows; plasma power 500 watt and gas pressure 16 torr ($\approx$2.13 kPa). H_2 flow rate 80 sccm and methane 20 sccm and the growth time was 3 min while the growth temperature was varied. The PL measurements were performed at room temperature under the excitation of a laser with wavelength of 325 nm.

Our samples are subjected to the investigations by Analytical scanning electron microscope JEOL JSM-6490LA with resolution (3 nm) and operating potential 30 kV, the energy dispersive X-ray analysis (EDX) which is attached to the electron microscope and 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.

3. Results and discussion

3.1. Scanning electron microscope

Fig. 1 represents the scanning electron microscope images of the carbon nanotube that have been prepared by microwave plasma-enhanced chemical vapor deposition on diatomite at different temperatures. It is clear that when the growth temperature was 400 °C there are no carbon nanotubes, but as the growth temperature increased the quantity of CNTs also increased and reaches a maximum amount when the growth temperature was 700 °C. As can be seen from Fig. 2 the CNTs are reasonably straight and extending normal to the surface of the substrate. The diameter of the CNTs as measured by the SEM was in the range of 40–80 nm where the length may reach to several tens of microns. The study of

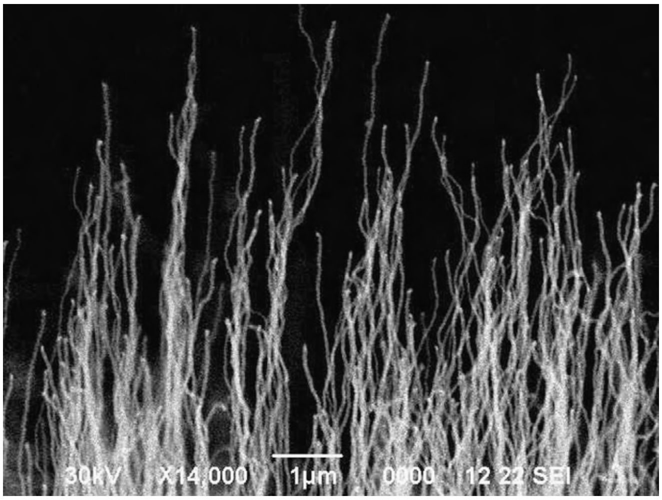

Fig. 2. Vertical carbon nanotubes on the diatomite at 700 °C, the white dots at the CNTs ends are due to the catalyst particles and indicating that the growth mechanism was through the tip mechanism.

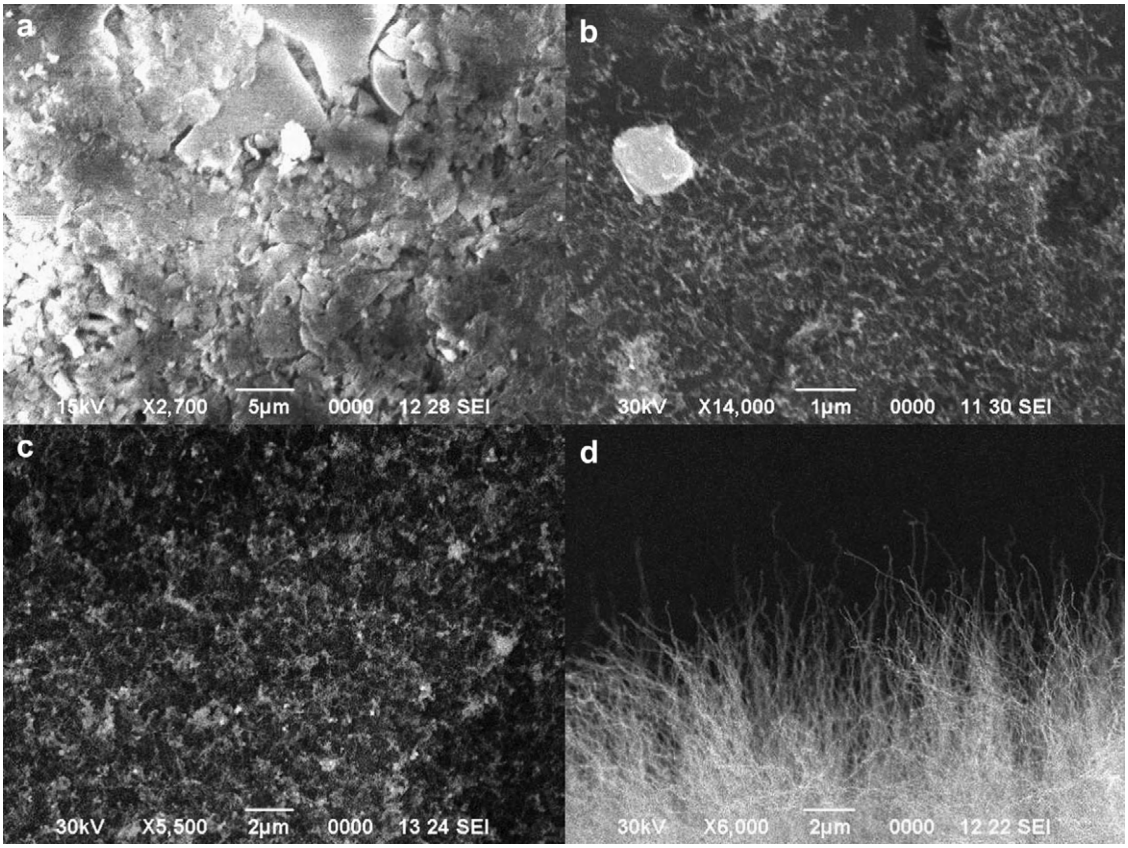

Fig. 1. Carbon nanotubes at different temperatures at a) 400 °C, b) 500 °C, c) 600 °C and d) 700 °C.

Please cite this article in press as: Duraia E-S, et al., Growth of carbon nanotubes on diatomite, Vacuum (2009), doi:10.1016/j.vacuum.2009.09.012

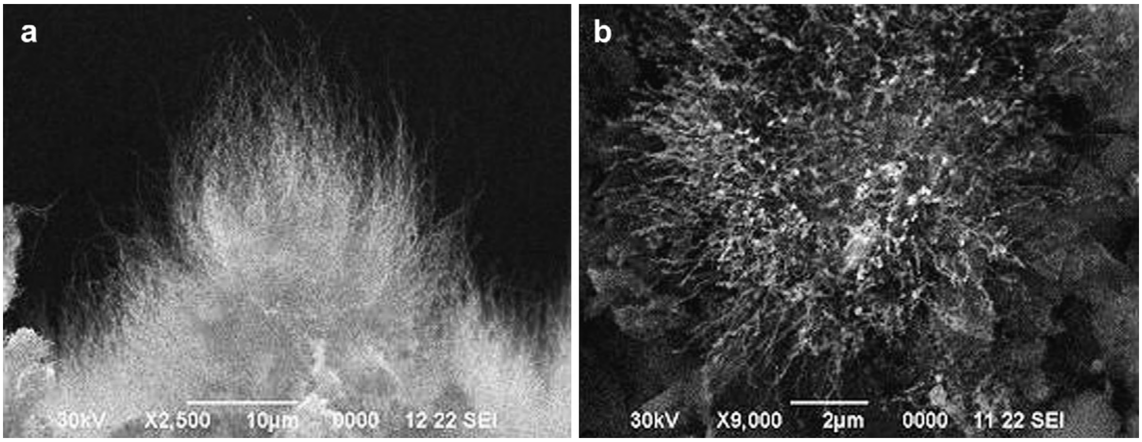

Fig. 3. The growth of CNTs in all directions from one catalyst particle.

the growth mechanism of carbon nanotubes would normally require a high resolution transmission electron microscope, TEM; however, in this case the use of SEM in our samples is enough to observe the catalyst particles at the tip of the CNTs. This is very important in understanding the growth mechanism of CNTs. The observation of the catalyst particles at the tips of the CNTs indicates that the growth mechanism is via the tip growth mechanism. In that mechanism due to the weak attraction between the catalyst and the substrate, the catalyst will leave the substrate and move up with the growing carbon nanotube. In Fig. 3 one can see that there are many CNTs that grow from one big circular catalyst particle. These CNTs are growing in all directions but at the same time perpendicular to the catalyst particle. This type of growth indicates that the catalyst was very active under the growth conditions utilized and this is very useful if a high quantity of CNTs is needed.

3.2. *Raman spectroscopy*

Raman spectroscopy is considered to be a very good method for CNTs characterization since the sample preparation is minimal moreover not time consuming and nondestructive. The first-order Raman spectrum of MWCNTs consists of bond stretching out-of-plane phonon modes in the low frequency region or radial breathing modes RBM [6], in-plane bond stretching motion of pairs of sp^2 hybridized carbon atoms (G mode) and in-plane breathing mode of A1 g symmetry due to the presence of six fold aromatic rings which is known as D mode [7]. Fig. 4 represents the typical Raman spectrum of the carbon nanotubes on diatomite at the temperatures 500 °C, 600 °C and 700 °C respectively. One can note that there are two basic intensive peaks at 1347 cm^{-1} (D band) and 1583 cm^{-1} (G-band). These peaks at approximately the same position were observed for all samples at all temperatures It well known that the ratio of the two bands (I_G/I_D) is directly proportional to the in-plane crystallite size until the material becomes nanocrystalline graphite [8]. From the ratio of integrated intensity La = 4.4 (I_G/I_D) nm [9,10] the crystallite average size La ~ 4.45 nm has been estimated. As we can see from the figure the ratio of (I_G/I_D) at the growth temperature 500 °C was 1.0118 and increases to 1.0180 at temperature 600 °C and deceases again as the temperature increased. 0 n the other hand at the low frequency mode or radial breathing mode one can note a number of peaks in the range

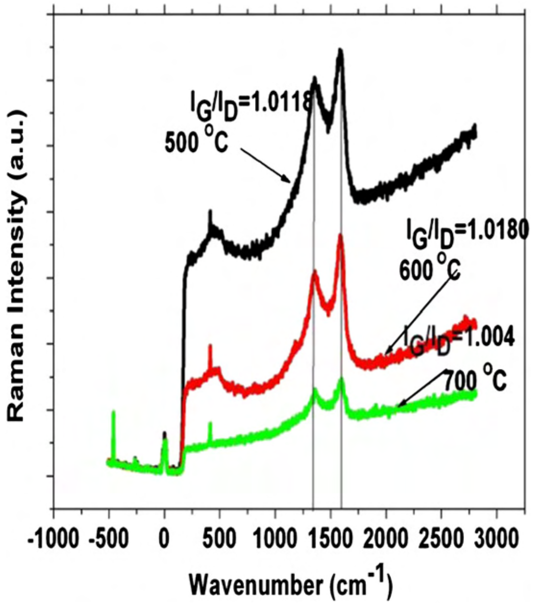

Fig. 4. Raman spectrum of the CNTs prepared on diatomite at different temperatures.

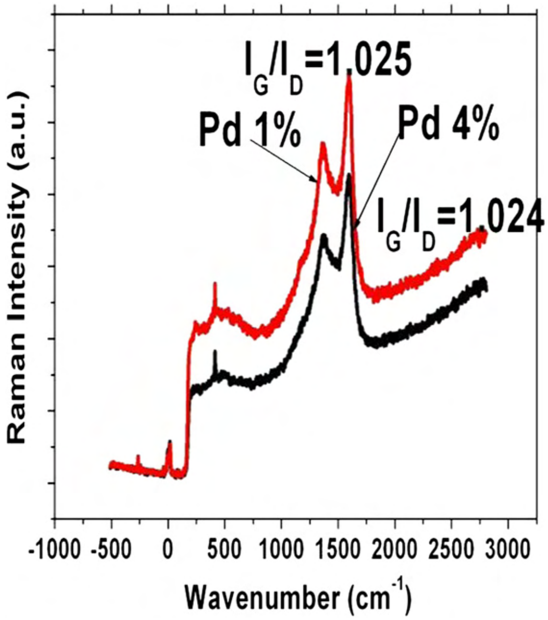

Fig. 5. Raman spectrum of the CNTs prepared on diatomite at different Pd concentrations.

Please cite this article in press as: Duraia E-S, et al., Growth of carbon nanotubes on diatomite, Vacuum (2009), doi:10.1016/j.vacuum.2009.09.012

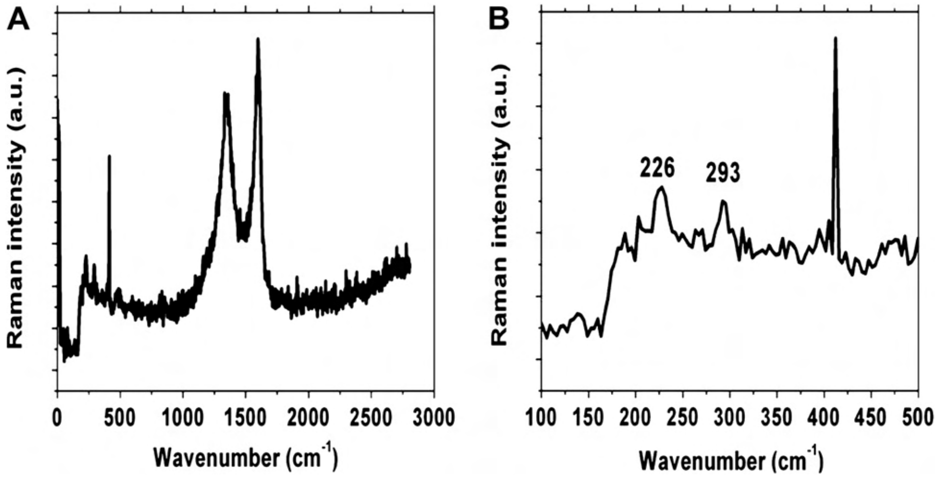

Fig. 6. A) Raman spectrum of the CNTs prepared on diatomite by using iron as a catalyst with concentration 10%. B) Magnification of the RBM part of SWCNT.

from 100 cm^{-1} to 500 cm^{-1}. These peaks are related to the single wall carbon nanotubes (SWCNTs). Fig. 5 represents Raman spectrum of CNTs at different catalyst concentrations (4%and 1%). The low catalyst concentration is better than the higher concentrations. Although there are a small difference in the value of the ratio (I_G/I_D), but the Raman intensity at the lower concentration is higher than that of higher concentration. Also at lower frequency range or RBM for the lower catalyst concentration there are many peaks in the range from 100 cm^{-1} to 500 cm^{-1} which are more intense than that of the higher concentration. Fe has been also used as a catalyst, Fig. 6 represents Raman spectrum for CNTs produced by using Fe as a catalyst with concentration 10%. The value of (I_G/I_D) was 1.004 which is lower than that of CNT's produced utilizing Pd as catalysts. The most important feature is the appearance of the RBM, there are several peaks in the range from 100 cm-1 to 500 cm-1 At a first-order approximation, if the relationship between the SWCNT diameter D and Raman shift ω, D (nm) = 248/ω (cm^{-1}) [11], is applied to the RBM in Fig. 6B, and then the numerical majority of SWCNTs are found to have a diameter about 1.093 nm, 0.846 nm for the peaks at 226 and 293 cm^{-1} respectively.

3.3. *Photoluminescence measurements*

Diatomite may be considered as a unique naturally occurring source of porous silica; which has many applications. The PL measurements were performed at room temperature under the excitation of a laser with wavelength of 325 nm. The laser beam was focused onto the sample with a very small spot size (of about 0.1 mm in diameter), and this in order to avoid local oxidation of the sample. The PL spectra of diatomite have been studied and found to contain two peaks one at 3.1 eV and a broad peak at 2.25 eV [12]. Fig. 7 represents the PL spectrum of the pure diatomite without any additions and before the growth of CNTs. There is a very wide peak that begins at 350 nm (3.53 eV) and ends at about 700 nm (1.76 eV) which covers approximately all the visible range and this indicate that there are a wide range of contributions to the photoluminescence spectrum. The photoluminescence spectrum of the CNTs on the diatomite produced at the growth temperature of 700 °C – is represented in the Fig. 8. There are two overlapping intense peaks near the ultraviolet range with the wavelengths 411 nm, 430 nm or 3 eV and 2.8 eV respectively. And there are two peaks with lower intensity in the infrared region at 830 nm and at 940 nm. Through the experiments it was observed that the photoluminescence intensity was very sensitive to the change in the angle of incidence as shown in Fig. 9. 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

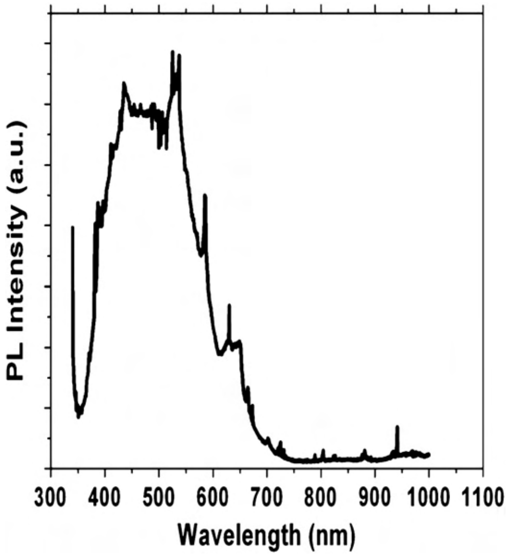

Fig. 7. Photoluminescence spectrum of pure diatomite.

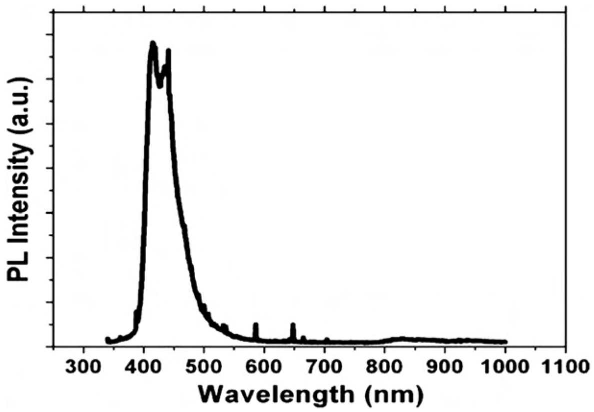

Fig. 8. Photoluminescence of CNTs on diatomite prepared at 700 °C.

Please cite this article in press as: Duraia E-S, et al., Growth of carbon nanotubes on diatomite, Vacuum (2009), doi:10.1016/j.vacuum.2009.09.012

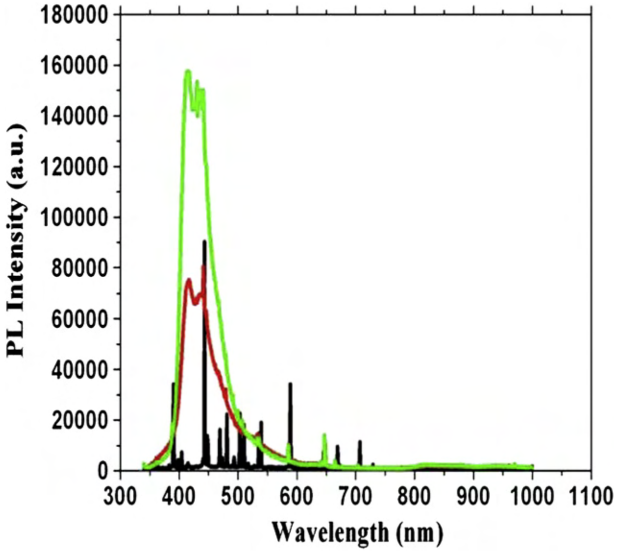

Fig. 9. Effect of the angle on the PL of diatomite-carbon nanotubes.

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 intensity is gradually decreased with the annealing temperature and completely disappeared after the annealing at 600 °C in air for 5 min.

4. Conclusion

In summary, vertical CNTs with average diameter 60 nm have been grown on diatomite by using microwave plasma-enhanced chemical vapor deposition. The effect of the growth temperature on the formation of the CNTs has also been studied. It was noted that the quantity of CNTs was increased as the temperature increased. Investigations by Raman spectroscopy supported the existence of the single wall carbon nanotubes at the lower temperature and lower catalyst concentrations. The photoluminescence measurements was made at the room temperature and showed two overlapping intensive peaks at 411 nm and 430 nm and these photoluminescence showed polarization dependence and completely disappeared after the annealing at 600 °C in air for 5 min.

References

[1] Kroto H, Heath J, Curl R, Samally R. Nature 1985;318:186.
[2] Ijima S. Nature (London) 1991;354:56.
[3] Journet C, Maser WK, Bernier P, Loiseau A, delaChapelle ML, Lefrant S, et al. Nature 1997;388:756.
[4] Thess A, Lee R, Nikolaev P, Dai HJ, Petit P, Robert J, et al. Science 1996;273:483.
[5] Mohamedbakr H, Burkitbaev M. Open Miner J 2009;3:12–6.
[6] Benoit J, Buisson J, Chauvet O, Godon C, Lefrant S. Phys Rev B 2002;66:73417.
[7] Dresselhaus M, Dresselhaus G, Saito R, Jono A. Phys Rep 2005;409:47–9.
[8] Tuinstra F, Koening J. J Chem Phys 1970;53:1126.
[9] Reich S, Thomsen C. Philos Trans R Soc Lond A 2004;362:2271–88.
[10] Jawhari T, Roid A, Casado J. Carbon 1995;33:1561–5.
[11] Jorio A, Saito R, Hafner JH, Lieber CM, Hunter M, McClure T, et al. Phys Rev Lett 2001;86:1118.
[12] Butcher K, Ferris J, Phillips M, Wintrebert-Fouquet M, Jong Wah Nemanja Jovanovic J, Vyverman W, et al. Mater Sci & Eng C 2005;25:658–63.

Please cite this article in press as: Duraia E-S, et al., Growth of carbon nanotubes on diatomite, Vacuum (2009), doi:10.1016/j.vacuum.2009.09.012