

Carbon Nanowalls grown by HFCVD on Glass Substrate

M. Ghoranneviss*

Plasma Physics Research Center, Science & Research Branch, Islamic Azad University, Tehran, Iran

P. Alizadeh Eslami

Chemical Faculty, Tehran North Branch, Islamic Azad University, Tehran, Iran

S. Nasiri Laheghi

Plasma Physics Research Center, Science & Research Branch, Islamic Azad University, Tehran, Iran

Abstract

Introduction: Self-assembled carbon nanostructures like carbon nanotubes (CNTs) and nanofibers have attracted much attention for several applications, such as gas storage, membranes for electrochemical energy storage, and field emitters. In addition, two-dimensional graphitic carbon structures, commonly referred to as carbon nanowalls (CNWs) or nanoflakes, are found attractive both as far as their structures, and their applications due to their high surface to volume ratios. Moreover, these structures have a great potential to act as metallic clusters supporting elements for electrochemical fuel cells. The morphologies of the metallic clusters supports have much effect on the chemical activity of the metallic clusters themselves. Also, the carbon nanowalls very sharp and thin edges being perpendicular to the substrate can act as field emitters.

Aim: This work concentrates on the growth of carbon nanowalls (CNWs) on a glass substrate coated with Fe nanocatalyst. Parameters affecting the growth of CNWs such as hydrocarbon gas, flow ratio, deposition time, and temperature are investigated.

Materials and Methods: In this paper, a glass substrate is coated with Fe nanocatalyst by low temperature plasma. Carbon nanostructures (two-dimensional carbon nanostructures, CNTs, and diamond nanocrystals) are grown on the Fe-glass substrate by hot filament chemical vapor deposition (HFCVD) using carbon sources such as acetylene (C_2H_2), methane (CH_4), and diluting the gases such as hydrogen (H_2) and ammonia (NH_3). Surface morphology of the substrate is observed by atomic force microscopy (AFM). Samples are characterized by scanning electron microscopy (SEM) and Raman spectroscopy.

Results: CNWs were obtained by the HFCVD by applying $C_2H_2/NH_3/H_2$ mixture (20:80:100 sccm) for 45 minutes, and at $600^\circ C$. Results show that diamond configuration of nanocrystals formed by HFCVD employing $CH_4/NH_3/H_2$ (20:80:100 sccm) for 45 minutes, and $600^\circ C$ substrate temperature. The results show that the increase of the deposition time from 45 to 60 minutes causes a decrease of crystallite size (L_a), and a distribution of CNWs on the surface. Increase of the C_2H_2 flow ratio renders an increase of L_a with high density of CNWs on the surface.

Conclusion: As one important conclusion in this work, is that the growth of CNWs, and diamond nanocrystals on the Fe-glass substrate depend on the hydrocarbon gas species in

*Corresponding Author

the fed gas. It is also determined that, an increase of the temperature from 600°C to 700°C causes the formation of the CNTs on the substrate.

Keywords: Carbon nanowalls, nanocrystalline Diamond, Hot Filament Chemical Vapor Deposition, Sputtering

Introduction

Self-assembled carbon nanostructures like carbon nanotubes (CNTs)^[1,2] and nanofibers^[3] have attracted much attention for several applications, such as gas storage, membranes for electrochemical energy storage, and field emitters.^[4-7] On the other hand, two dimensional graphitic carbon structures, commonly referred to as carbon nanowalls (CNWs) or nanoflakes, are interesting for several possible applications due to their large surface to volume ratio. In particular, they have shown a potential as functional supports of metallic clusters in electrochemical fuel cells where different carbon nanowalls (CNWs) morphologies were observed to have a large effect on the chemical activation of the supported metallic clusters.^[8,9] Moreover, their very sharp and thin edges perpendicular to the substrate can act as field emitters.^[10] A transmission electron microscopy study was revealed that CNWs consist of few graphene sheets stacked together, like thin graphite flakes.^[11-13] The CNWs have been grown vertically on the substrate with catalyst using microwave plasma enhance chemical vapor deposition (PE-CVD)^[14] or without catalyst using radio-frequency (rf) PECVD assisted by H radical injection.^[15] Recently, Escobar and coworkers reported the effect of acetylene pressure on nanotubes characteristics by CVD on Fe nano particles at 180 torr.^[16]

In this paper, the glass substrate was coated with Fe nanocatalyst by low temperature plasma. Carbon nanostructures (two-dimensional carbon nanostructures, CNTs and nanocrystalline diamond) have been grown on the Fe/glass substrate by HFCVD with carbon source such as acetylene (C₂H₂), methane (CH₄) and dilution gas such as hydrogen (H₂) and ammonia (NH₃). We have studied some of effective parameters such as type of hydrocarbon gas, flow ratio of C₂H₂, time and substrate temperature in the growth of CNWs. The samples were analyzed for characterization of surface morphology and roughness parameters of the substrate, alignment, distribution and type of carbon nanostructures. These characterizations were measured by atomic force microscopy (AFM), scanning electron microscope (SEM) and Raman spectroscopy.

Experimental method

Substrate Preparation

Fe nanolayer with 20 nm thickness was deposited on the microscopic glass slides (5 mm × 5 mm × 0.9 mm) as catalyst by low temperature plasma. The instrument used in this experiment was direct current magnetron sputtering (DC-MS) system and consisted of a cylindrical glass tube and two Fe co-axial cylinders were made as cathode (inner one, 30 mm diameter and 200 mm in length) and anode (outer one, with 100 mm diameter and 200 mm in length) in this chamber. Nitrogen (N₂) was selected as a sputtering gas and operation pressure was 0.03 torr. The substrates were cleaned by ultrasonic vibration with acetone, ethanol and deionized water to remove all contaminants. For Fe Coating, uniform magnetic field from outside was 400 Gauss. Applied voltage between anode and cathode was about 900V and observed current was 120mA. Microscope glass slide as a substrate was fixed on the anode. Distance between target and substrate was about 30mm. Surface morphology of this film was observed with AFM (Autoprobe cp, Park Scientific Instrument).

Growth of Carbon Nanowalls

Fe/glass substrate puts in the center of the furnace. To avoid the catalyst oxidation, base pressure of reaction chamber was 10⁻⁵ torr and argon (Ar) gas with 200 standard cubic

centimeters per minute (sccm) was fed inside the chamber of HFCVD to 1 torr, then substrate temperature and filament temperature were increased to 350°C and 1200°C, respectively. For etching of the substrate closed Ar valve and open H₂ with 100 (sccm) into the chamber and substrate temperature reached to 500 °C, time of etching was 10 minutes. Combination of C₂H₂/NH₃/H₂ with 20:80:100 (sccm) flow ratio, and in another experiment CH₄/NH₃/H₂ with 20:80:100 (sccm) flow ratio was fed into reaction chamber, separately. Reaction time and substrate temperature for the growth was 45 minutes in 600°C for substrate temperature and 1800°C for filament temperature. In another experiments, we change the condition by gas flow, time and substrate temperature from 20 to 48 (sccm), 45 to 60 minutes and 600°C to 700°C, separately. The carbon nanostructures obtained in this way were analyzed with SEM (XL30, 15-30.kV, Philips Company) and Raman spectroscopy (Thermo Nicolet Crop. Madison, Wisconsin 53711, USA) with a fixed wave length of 1064 nm.

Results and Discussion

Surface morphology of Fe nanolayer on the glass was observed using AFM and was shown in Fig.1. Average roughness of Fe/glass is 1.02 Å.

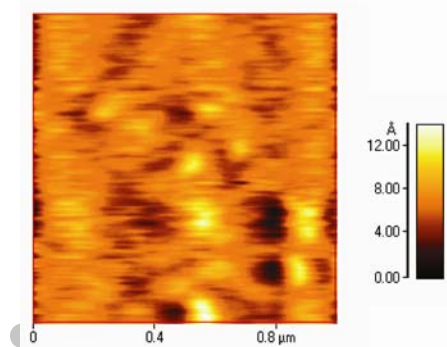


Fig. 1- AFM analysis of Fe nanolayers on the glass substrate and its roughness.

The SEM micrographs in Fig. 2 show the morphologies of carbon nanostructures grown on the Fe nanocatalyst coated on the glass substrate. CNWs were obtained by HFCVD by applying C₂H₂/NH₃/H₂ (20:80:100 sccm) for 45 minutes at 10 torr pressure in the 600°C. Fig. 2(a) shows SEM image of these CNWs. This image shows that two dimensional carbon nanosheets were grown vertically on the substrate, forming a unique nanostructure similar to a petal like. CNWs were thin and their thickness was less than 28 nm. Fig. 2(b), shows the typical SEM image of diamond nanocrystals fabricated by HFCVD employing CH₄/NH₃/H₂ (20:80:100 sccm) for 45 minutes at 10 torr pressure, with substrate temperature 600°C. This image shows that nanocrystalline diamonds were grown on the substrate, and randomly oriented diamond crystals are still evident and average length of crystalline diamond grown was about 100 nm. In the absence of CH₄ nanocrystalline diamonds were grown on the glass surface are covered by Fe nanocatalyst. Fig 2(c) shows the SEM image of high density CNWs grown by HFCVD employing C₂H₂/NH₃/H₂ (48:80:100 sccm) for 45min at 10 torr pressure. Temperature of substrate was 600°C. Thickness of the CNWs was increased. Finally we have reproduced growth of CNWs film by HFCVD in two new conditions at first in 60 min and second at substrate temperature 700°C.

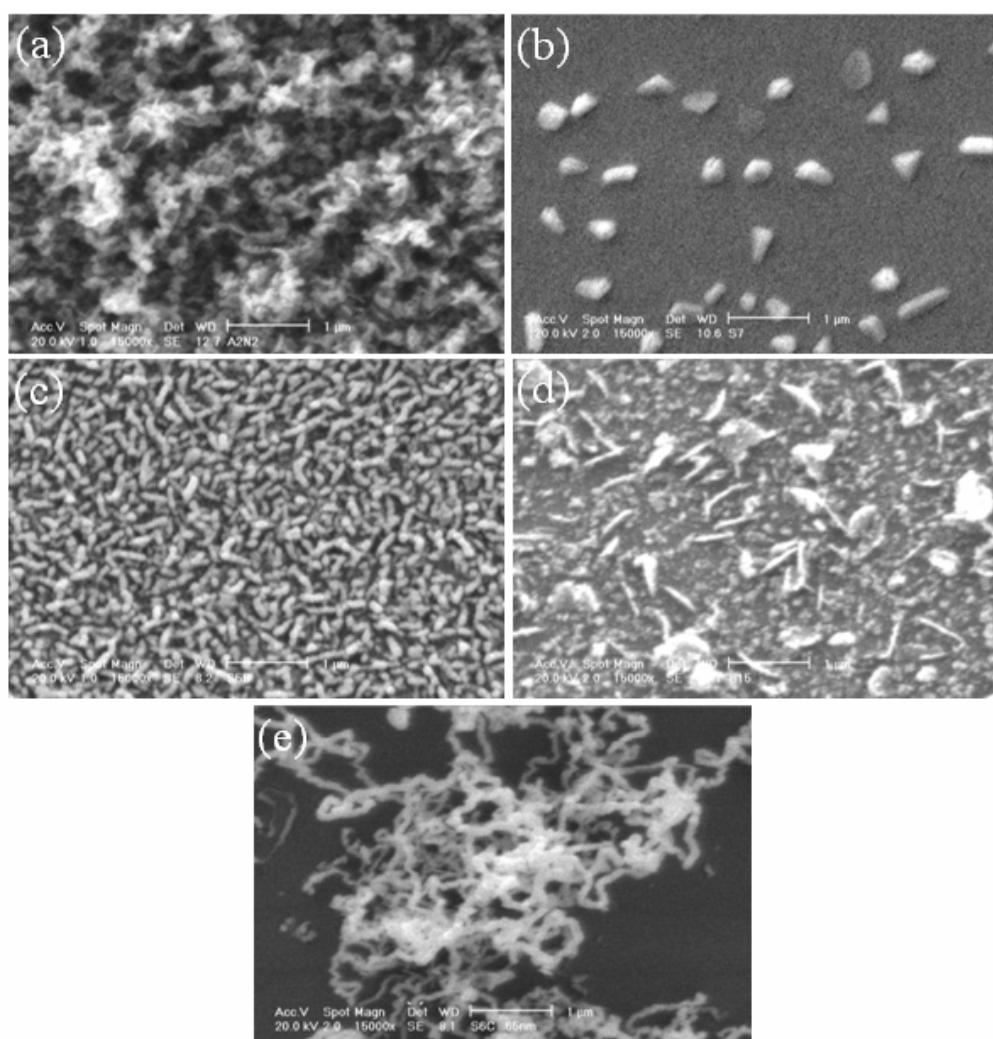


Fig.2- SEM images of the carbon nanostructures grown on glass substrate coated with Fe nanocatalys with: (a) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. in $600^\circ C$; (b) $CH_4/NH_3/H_2$ (20:80:100 sccm) for 45min. in $600^\circ C$; (c) $C_2H_2/NH_3/H_2$ (48:80:100 sccm) for 45min. in $600^\circ C$; (d) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 60 min. in $600^\circ C$; (e) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. in $700^\circ C$

Fig.2 (d) shows the SEM image of CNWs obtained by HFCVD employing $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 60 min at 10 torr pressure and $600^\circ C$ substrate temperature. Thickness of the CNWs was increased. But the distribution of CNWs in the surface was decreased. Fig.2 (e) shows the SEM image of CNTs obtained by HFCVD employing $C_2H_2/NH_3/H_2$ (20:80:100 sccm) mixture for 45 min at 10 torr pressure and $700^\circ C$ substrate temperature. This image shows that CNTs with 65 nm in diameter were fabricated on the substrate. The limits of the process for growth of CNWs on Fe coated on glass were investigated by different process parameters: substrate temperature, time with different gas flow. The results were found for substrate temperatures starting a lower limit about $600^\circ C$, and a $C_2H_2: NH_3: H_2$ precursor gas mixture. After reaction high Ar flow rate is necessary to minimize the unwanted reaction and to prevent ionization of species.

The Raman spectra of the carbon nanostructures grown on the glass substrate coated with Fe nanocatalyst with different parameters are shown in Fig. 3. Generally three Raman bands can be identified. The D-band around 1320 cm^{-1} , the G-band around 1580 cm^{-1} and D'-band

around 1610 cm^{-1} . As shown in Fig. 3(a), the Raman spectrum for CNWs was found to have G band peak at 1580 cm^{-1} , indicating the formation of a graphitized structure and D band peak at 1320 cm^{-1} , corresponding to the disorder-induced phonon mode. The G and D peaks are comparable in intensity. It should be noted that the G band peak is accompanied by a shoulder peak at 1610 cm^{-1} (D band). This shoulder peak is associated with finite-size graphite crystals.^[17,18] The strong D band peak suggests a more nanocrystalline structure and presence at graphene edges and defects such as distortion, vacancies and straining to graphitic lattices which are prevalent features of CNWs. The crystallite size La stems in I_D/I_G intensity ratio. The empirical formula $La=44/(I_D/I_G)$ has been successfully used for Raman spectra taken with the excitation energies around 514.5 nm ,^[19,20] although the I_D/I_G intensity ratio strictly depends on the Raman excitation energy.^[21,22] Therefore, the above formula was also employed for Raman spectra with 1064 nm excitation energy in the present experiments. From these estimations, it is found that the average crystallite sizes La in the CNWs obtained in the present experiments are 19.36 \AA . In Fig. 3b, Raman spectrum shows three peaks located at 1350 cm^{-1} , 1410 cm^{-1} and the small graphite peak at 1590 cm^{-1} indicates that the films grown by HFCVD were high quality diamond and that nucleation and growth of diamond emphasized on Fe coated on glass substrate. In the Raman bands, the D band is around 1410 cm^{-1} and the G band is around 1590 cm^{-1} . Fig. 3(c) shows three Raman bands. The D-band around 1320 cm^{-1} , the G-band around 1580 cm^{-1} and D'-band around 1610 cm^{-1} . These images show that two dimensional carbon sheets were grown vertically on the substrate. With increasing flow rate of C_2H_2 (48 sccm) the thickness of CNWs increase. Average crystallite sizes La in the CNWs obtained in the present experiment is 51.5 \AA . In Fig. 3(d) Raman bands can be identified, The D-band around 1320 cm^{-1} , the G-band around 1580 cm^{-1} and D'-band around 1610 cm^{-1} . This image shows that two dimensional carbon nanosheets were grown vertically on the substrate similar to growth in 45 min . In this condition thickness of the CNWs was increased. Average crystallite sizes La in the CNWs obtained in the present experiment is 28.75 \AA . Fig. 3(e) shows strong peaks located at around 1320 and 1585 cm^{-1} . Strong peaks located at around 1330 and 1590 cm^{-1} correspond to the disorder-induced D-band and the G-band of multiwall CNTs, respectively.^[23] The broad G-band graphite peak shows the presence of tubular structure in the CNTs.^[24] Sufficient dilution of C_2H_2 in H_2 was necessary for successful CNWs growth as mentioned in previous studies by other authors, e.g. for etching unwanted amorphous carbon^[25] and reducing C_2H_2 reactivity. We have found that an optimum $\text{NH}_3:\text{H}_2:\text{C}_2\text{H}_2$ precursor gas ratio is $4:5:1$.

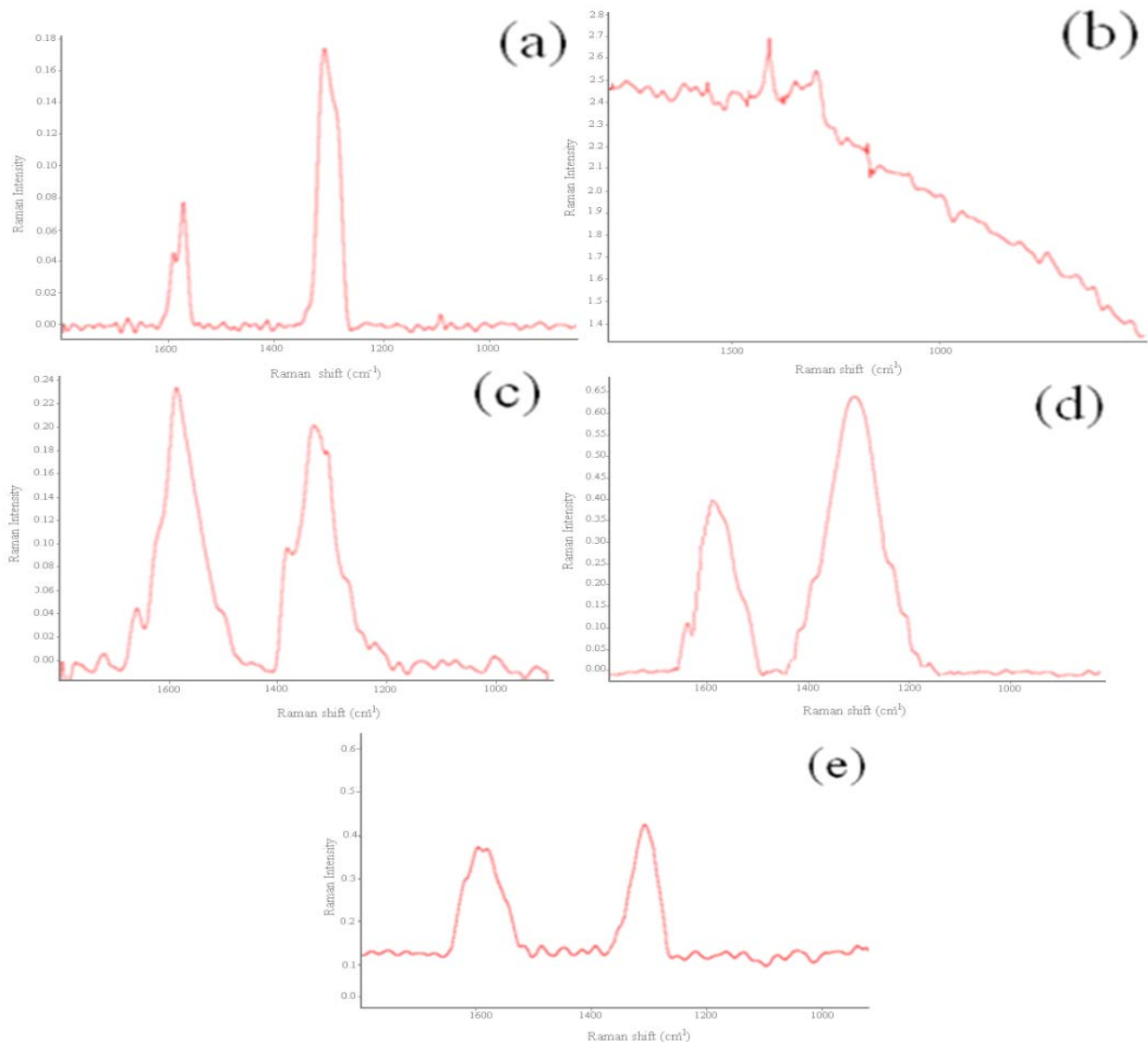


Fig.3-Raman spectrum of the carbon nanostructures grown on glass substrate coated with Fe nanocatalyst with: (a) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. in $600^\circ C$; (b) $CH_4/NH_3/H_2$ (20:80:100 sccm) for 45min. in $600^\circ C$; (c) $C_2H_2/NH_3/H_2$ (48:80:100 sccm) for 45min. in $600^\circ C$; (d) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 60 min. in $600^\circ C$; (e) $C_2H_2/NH_3/H_2$ (20:80:100 sccm) for 45min. in $700^\circ C$.

Our experiments indicate that the presence of a catalyst is a necessary condition for the growth, since no CNWs could be synthesized in the absence of a Fe catalyst. A qualitative analysis of the carbon coating is performed with Raman spectroscopy. Each spectrum shows three characteristic carbon bands, i.e., the disorder induced D-band around 1350 cm^{-1} , the G band around 1580 cm^{-1} that is related to in-plane sp^2 vibrations, and the disorder induced D'-band around 1610 cm^{-1} [18,26–29]. For a qualitative analysis of graphite-like structures, the intensity ratio of the D-band in compared with the G-band is measured and denoted as the R-value: $R = I_D/I_G$. [28] CNWs usually suffer from defects and are well-known for their relatively large R-value, exceeding unity [18, 24] and while pure CNTs and highly ordered graphite can have R-values close to zero. [27–29] The Raman spectra of CNWs showed $R=2.27, 0.85, 1.53$

for Figs (2a, 2c, 2d) respectively. These results indicate that the CNWs are somewhat more ordered with respect to their sp^2 structure. We applied equation of $La=44/ (I_D/ I_G)^{[19-20]}$ to investigate the crystallite size of the CNWs. These results show that increase of time deposition from 45 to 60 min causes to decrease of La and distribution of CNWs in surface. Increase of C_2H_2 flow ratio causes to increase of La with high density of CNWs in surface (as shown as SEM images). Increase of substrate temperature from $600^\circ C$ to $700^\circ C$ causes to fabrication of CNTs on the substrate.

Conclusions

In this paper, high surface area CNWs, CNTs and diamond nanocrystals can be synthesized by HFCVD system in 10 torr pressure. These carbon nanostructures were fabricated on glass where Fe was deposited by DC-MS as catalyst. C_2H_2 and CH_4 were used as a carbon source. H_2 and NH_3 were applied as a dilution gas. To conclude:

- (i) The SEM characterization gives the experimental conditions permitting the growth of CNWs and diamond nanocrystals depending on the hydrocarbon gas species in the feed gas.
- (ii) An increase in the C_2H_2 flow ratio causes to increase crystallite size (La) and density of CNWs in surface.
- (iii) An increase in the time of reaction causes to decrease distribution of CNWs in surface and increase the crystallite size (La).
- (iv) An increase of substrate temperature from $600^\circ C$ to $700^\circ C$ causes to fabrication of CNTs on the substrate.

Archive of SID

References:

1. Bower, C., Zhu, W., Jin, S., and Zhou, O., *Appl. Phys. Lett.*, **77**, 830 (2000).
2. Bower C., Zhou, O., Zhu, W., Werder, D.J., and Jin, S., *Appl. Phys. Lett.*, **77**, 2767 (2000).
3. Caughman, J.B.O., Baylor, L.R., Gulliom, M.A., Merkulov, V.I., Lowndes, D. H., and Allard, L.F., *Appl. Phys. Lett.*, **83**, 1207 (2003).
4. Rinzler, A.G., Hafner, J.H., Nikolaev, P., Lou, L., Kim, S.G., Tomanek, D., Nordlander, P., and Cobert, D.T., Smalley, R.E., *Science*, **269**, 1550 (1995).
5. Dillon, A.C., Jones, K.M., Bekkedahl, T.A., Kiang, C.H., Bethune, D.S., and Heben, M.J., *Nature*, **386**, 377 (1997).
6. Che, G., Lakshmi, B.B., Fisher, E.R., and Martin, C.R., *Nature*, **393**, 346 (1998).
7. de Heer, W.A., Chatelain, A., and Ugarte, D., *Science*, **270**, 1179 (1995).
8. Giorgi, L., Makris, Th.D., Giorgi, R., Lisi, N., and Salernitano, E., *Electrochemical properties of carbon nanowalls synthesized by HF-CVD. Sens. Actuators B*, **126**, 144 (2007).
9. Shang, N.G., Au, F.C.K., Meng, X.M., Lee, C.S., Bello, I., and Lee, S.T., *Chem. Phys. Lett.*, **358**, 187 (2002).
10. Chen, C.C., Chen, C.Fu., Lee, I.H., and Lin, C.L., *Diamond Relat. Mater.*, **14**, 1897 (2005).
11. Hiramatsu, M., and Hori, M., *J. pn. J. Appl Phys. B*, **45**(6), 5522 (2006).
12. Nishimura, K.J., and Hiraki, A., *I. E. I. C. E. Trans. Electron. E*, **86-C** (5), 821 (2003).
13. Wu, Y., Yang, B., Zong, B., Sun, H., Shen, Z., and Feng, Y., *J. Mater Chem.*, **144**, 69 (2004).
14. Wu, Y., Qiao, P., Chong, T., and Shen, Z., *Adv. Mater. (Weinheim, Ger.)*, **14**, 64 (2002).
15. Hiramatsu, M., Shiji, K., Amano, H., and Hori, M., *Appl. Phys. Lett.*, **84**, 4708 (2004).
16. Escobar, M., Moreno, M.S., Candal, R.J., Rubiolo, G.H., and Goyanes, S., *Appl. Surf. Sci.*, **254**, 251 (2007).
17. Yu, J., Zhang, Q., Ahn, J., Yoon, S.F., Rusli, Y.J.Li., Gan, B., and Tan, K.H., *Diamond Relat. Mater.*, **10**, 2157 (2001).
18. Kurita, S., Yoshimura, A., Kawamoto, H., Vchida, T., and Nakai, H., *J. Appl. phys.*, **97**, 104320 (2005).
19. Tuinstra, F., and Koenig, J.L., *J. Chem. Phys.*, **53**, 1126 (1970).
20. Knight, D.S., and White, W. B., *J. Mater. Res.*, **4**, 385 (1988).
21. Mernagh, T.P., Cooney, R.P., and Johnson, R.A., *Carbon*, **22**, 39 (1984).
22. Pócsik, I., Hundhausen, M., Koós, M., and Ley, L., *J. Non-Cryst. Solids*, **7**(30), 1083 (1998).
23. Rao, A.M., Baik, K., Bang, J., Lee, S., and Sigmund, W., *Solid State Commun.*, **129**, 583 (2004).
24. Zhu, S., Su, C., Cochrane, J.C., Lechoczky, S., Cui, Y., and Burger, A., *J. Cryst. Growth*, **234**, 584 (2002).
25. Park, S., and Walser, R.M., *Carbon*, **23**, 701 (1985).
26. Ni, Z.H., Fan, H.M., Feng, Y.P., Shen, Z.X., Yang, B.J., and Wu, Y.H., *J. Chem. Phys.*, **124**, 204703 (2006).
27. Kastner, J., Pichler, T., Kuzmany, H., Curran, S., Blau, W., Weldon, D.N., Delamesiere, M., Draper, S., and Zandbergen, H., *Chem. Phys. Lett.*, **221**, 53 (1994).
28. Dresselhaus, M.S., Dresselhaus, G., Jorio, A., Souza Filho, A.G., and Saito, R., *Carbon*, **40**, 2043 (2002).
29. Dresselhaus, M.S., Dresselhaus, Saito, R., and Jorio, A., *Phys Reports*, **409**, 47 (2005).