Journal of the Korean Institute of Illuminating and Electrical Installation Engineers Vol. 23, No.7, pp. 8~13 July 2009 (23-7-2)

Fundamental Study of CNTs Fabrication for Charge Storable Electrode using RF-PECVD System

Ki-Young Jung* · Hyuk-Moon Kwon · Jin-Woo Ahn · Dong-Hoon Lee · Won-Zoo Park · Youl-Moon Sung**

Abstract

Plasma enhanced chemical vapor deposition (PECVD) is commonly used for Carbon nanotubes (CNTs) fabrication, and the process can easily be applied to industrial production lines. In this works, we developed novel magnetized radio frequency PECVD system for one line process of CNTs fabrication for charge storable electrode application. The system incorporates aspects of physical and chemical vapor deposition using capacitive coupled RF plasma and magnetic confinement coils. Using this magnetized RF-PECVD system, we firstly deposited Fe layer (about 200[nm]) on Si substrate by sputter method at the temperature of 300[℃] and hence prepared CNTs on the Fe catalyst layer and investigated fundamental properties by scanning electron microscopy (SEM) and Raman spectroscopy (RS). High-density, aligned CNTs can be grown on Fe/Si substrates at the temperature of 600[℃] or less.

Key Words : Plasma enhanced chemical vapor deposition, Carbon nanotubes, RF plasma, Fe catalyst

1. Introduction

Reports of the synthesis and identification of carbon nanotubes (CNTs), multi-walled [1] and single-walled [2], have excited great interest in the field of carbon and related materials studies. Extraordinary properties, such as electronic [3] and mechanical [4] properties, have been performed both theoretically and experimentally. It has been important issue to search for new processing techniques, especially in the low temperature regime, which can produce high-quality CNTs in large quantities, while allowing control of the fabrication process with ease and precision. A number of techniques have been used to synthesize CNTs including arc discharge method [1-2], chemical vapour deposition (CVD) [5], laser ablation [6], etc. However, it has been shown that plasma enhanced chemical vapor deposition (PECVD) [7] is one of the most promising techniques for low temperature deposition, high deposition rate, cleanliness and low particulate levels. For low temperature deposition the operating gases need to be activated using microwave, laser, radio frequency (RF) or DC plasma to achieve

* Main author : Kyungsung University
** Corresponding author : Associate Professor in Kyungsung University
Tel : +82-51-6630-4777, Fax : +82-51-624-5980
E-mail : ymsung@ks.ac.kr
Date of submit : 2008. 12. 9
First assessment : 2008. 12. 17
Completion of assessment : 2008. 12. 30

respectable growth rates. Unless this enhanced precursor activation, extreme substrate temperatures are required and this severely limits the number of potential applications. With these considerations in mind, an magnetized radio frequency plasma enhanced chemical vapor deposition (magnetized RF-PECVD) apparatus has been set up in an effort to seek new processing routes for high-quality and high-efficiency CNTs production for charge storable electrode application. This new system incorporates aspects of physical and chemical vapor deposition using capacitive coupled RF plasma production technology and magnetic confinement coils. The capacitive coupled RF plasma source plays a role as sputtering for Fe catalyst layer formation and CVD for CNTs fabrication through a single line process. A magnetic confinement coils were incorporated to increase the plasma density around substrate region. The confined high-density plasma with magnetic field could affect the properties of CNTs in a beneficial way. In this study, CNTs properties, produced using novel magnetized RF plasma enhanced CVD (magnetized PF-PECVD) system, were investigated.

2. System geometry and description

The magnetized RF-PECVD system used to perform CNTs fabrication consisted of magnetic coils for plasma confinement, biased and heated substrate and assembly reactor chamber with a RF plasma generator and vacuum pumping system and is shown in Fig. 1. The plasma reactor comprised a water-cooled non-magnetic circular stainless steel chamber with quartz windows, which allow us to measure optical emission spectra of the RF discharge plasma. The inner diameter of the chamber was 250[mm]. In order to prevent needless plasma diffusion to the chamber wall and thus, to enhance plasma density around substrate region, the magnetic field was formed in the reaction zone. Two coils, shown as coils 1 and 2 in Fig. 1, were placed coaxially surrounding the chamber. The currents in coils 1 and 2 (I_1 and I_2, respectively) flew in the same direction. When the current of the two coils were set as $I_1=I_2=60$[A], the magnetic field strength at the center of the chamber was about B=250 Gauss. The heated substrate was placed at a distance of 60[mm] from the powered electrode (Fe cathode), and electrically isolated from the grounded chamber wall in order to apply a dc bias voltage. The substrates were pre-cleaned prior to entry into the vacuum system where they were subjected to additional plasma cleaning in argon plasma prior to deposition. The plasma cleaning was carried out at 0.1[Torr] with -300[V] DC bias voltage at the substrate. The operating gases, such as CH_4, N_2 and/or O_2, were introduced into the reactor with a single gas delivery line. An RF power supply and matching network was used to generate the

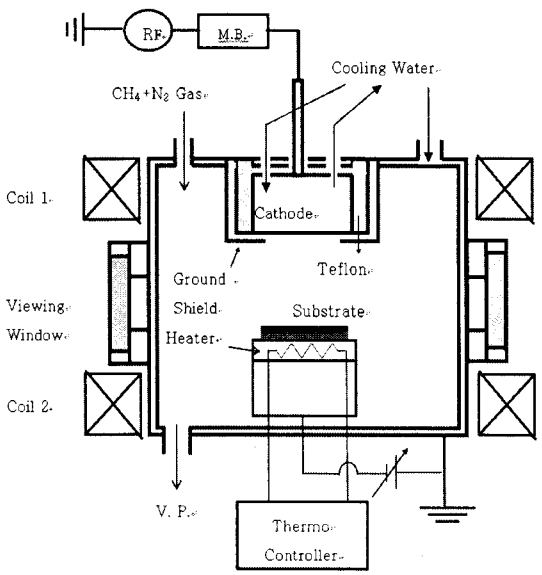


Fig. 1. Experimental apparatus

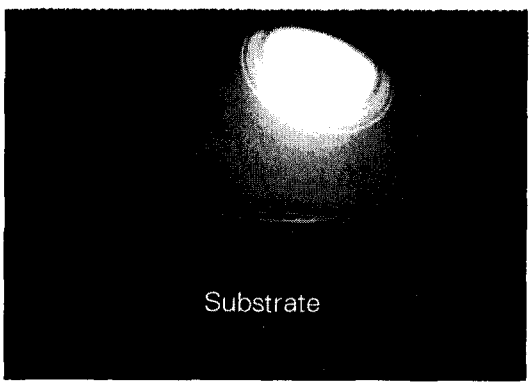
plasma between the two electrodes. Reflected power was always kept to below 10[W]. The CNTs produced were characterized using a variety of analytical methods.

3. Experimental procedure

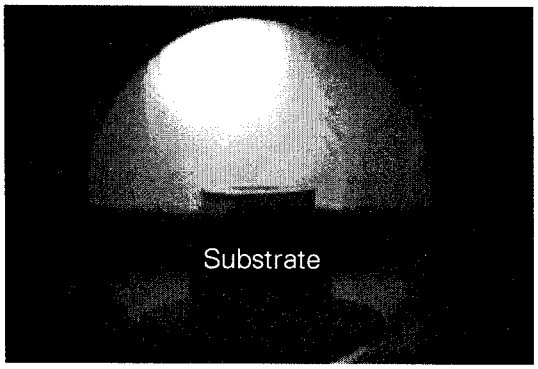
High quality single and multi-walled CNTs can be synthesized on adequate catalysts, and their size and distribution decide those of CNTs. Due to their active catalytic function, Fe catalysts serve as the nucleation sites for the growth of CNTs. A Fe catalyst layer of about 200[nm] thick was deposited from the Fe target on p-type Si (100) wafer by using the RF sputter method. The sputtering conditions can be optimized as follows. The Fe film was prepared in Ar gas pressure of 5.0×10^{-2}[Torr], the substrate temperature of 300 [℃], RF power of 500[W] and deposition time of 30[min]. The p-type Si (100) wafer having the Fe film of about 200[nm] thick was put on the stainless substrate stage. And hence, the plasma chamber was pumped down to a base pressure of 5.0×10^{-3}[Torr] by a rotary pump, and was purged for a few minutes with flowing nitrogen gas to carry out plasma surface treatment on the Fe catalyst layer. The formation of uniformly distributed high-density nano-sized catalysts is very important for high quality CNT synthesis because that each nano-scale Fe particles work as active catalysts for nucleation of CNTs. Therefore, the plasma surface treatment was carried out in order to form the nano-scale Fe catalysts using the magnetized RF plasma. In this case, the RF power was set at 400[W], while keeping the gas pressure at 5[Torr]. The substrate temperature and plama treatment time were set at 600[℃] and 10 min, respectively. Also, the magnetic flux density near the substrate surface was about 250 G. By introducing the magnetic field to the electrode space, the plasma generated intensively near the target region spreads towards the substrate along the magnetic field line, and thus the Fe layer is subjected to a flux of bombarding ions sufficient to cause changes in the surface structure. Regarding the CNT synthesis on optimally prepared Fe catalysts, the fabrication conditions were summarized as follows. The CNT was prepared in a mixture gas of 80[%] CH_4 and 20[%] N_2 at a pressure of 5[Torr], Fe/Si substrate temperature of 600[℃] and RF power of 600[W]. The magnetic flux density near the substrate region was about 250[G]. Deposition process was continued for 30[min]. The CNTs samples were evaluated using scanning electron microscopy (SEM) and Raman spectroscopy (RS).

4. Results and discussion

Figures 2(a) and 2(b) show the images of RF discharge taken for N_2 - CH_4 (20[%]) gas mixtures with RF power of 300[W] (a) and 600[W] (b). The total gas pressure is 0.5[Torr]. A Fe/Si wafer 50[mm] in diameter is used as a substrate, which is located on the anode in the CVD reactor chamber. The optical emission spectra in these conditions were also observed by CCD camera.



(a) N_2 - CH_4 (20[%]), PRF=300[W]

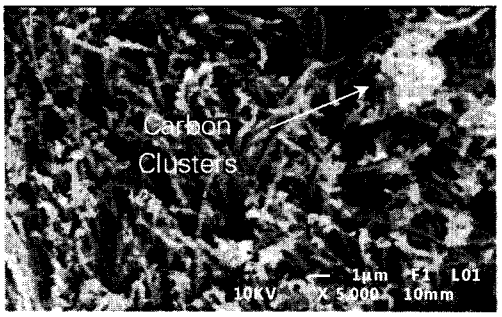


(a) N_2 - CH_4 (20[%]), PRF=600[W]

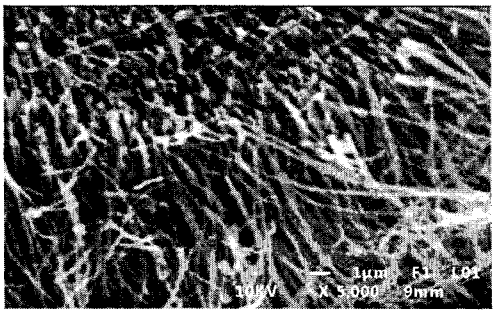
Fig. 2. RF plasma images taken for N2-CH4 (20[%]) gas mixtures with RF power of 300[W] (a) and 600[W] (b).

In the spectrum of Fig. 2 (a), one can observe the characteristic emission of CH radicals (390 and 430[nm]) and C_2 components (515 and 560[nm]). By performing spectral measurements in different plasma areas, we find that intensities of N_2-related optical emission spectral lines are nearly independent of position, whereas intensities of optical emission spectral lines associated with CH and C_2 are significantly higher near the plasma periphery areas. When the RF power exceeds about 500[W], the intense orange - yellow emission is observed in the top part of the discharge plasma periphery.

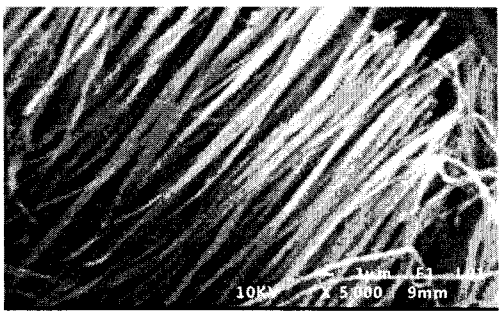
Fig. 3a, 3b and 3c show the SEM images of CNTs synthesized using Magnetized RF-PECVD on Fe catalysts for N_2 - CH_4 (20[%]) gas mixtures with RF power of 300[W] (a), 450[W] (b) and 600[W] (c). As shown in Fig. 3(c), high density CNTs with a length of 20[μm] grew on the Fe/Si substrate. The synthesis rate was approximately 500[nm/min]. It was found, from the results of Fig. 3b, that some carbonaceous particles or clusters were observed in CNTs, which were grown at RF power of 450[W]. The carbonaceous particles and clusters were formed when the RF power decreased below 300[W], and this did not depend on the substrate temperature.



(a) N_2 - CH_4 (20[%]), PRF=300[W]



(b) N_2 - CH_4 (20[%]), PRF=450[W]



(c) N_2 - CH_4 (20[%]), PRF=600[W]

Fig. 3. SEM images of CNTs synthesized using Magnetized RF-PECVD for N_2 - CH_4 (20[%]) gas mixtures with RF power of 300[W] (a), 450[W] (b) and 600[W] (c)

Figure 4 shows the single phonon (first order) Raman spectra, which were obtained using visible photons (e.g. 514.5[nm] from the Ar^+ ion laser) focused on CNTs samples with a beam size of 20[mm] using a Raman microscope. The result

shows a microcrystalline graphite at 1349.8 [cm^{-1}](D-band) and a crystalline graphite at 1575.3[cm^{-1}](G-band), the latter indicating the formation of graphene CNTs. The peak at 1349.8[cm^{-1}] has been known to be attributed to the carbonaceous particles, defects in the curved graphitic sheet and tube ends. The intensity of D-band peak is lower than that of the G-band. This fact shows that there were few carbonaceous particles or clusters in the CNTs synthesized in this work. This is in agreement with the observations in the SEM photographs of Fig. 3, and implies that high quality CNTs have been also synthesized in this work.

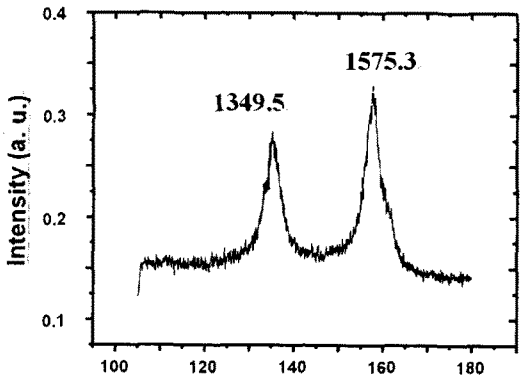


Fig. 4. Raman spectra on CNTs samples prepared by the magnetized RF-PECVD system

5. Summary

A magnetized RF-PECVD system was newly suggested for one line process of CNTs fabrication, and some preliminary results were investigated. The system incorporates aspects of physical and chemical vapor deposition using capacitive coupled RF plasma and magnetic confinement coils. Using this magnetized RF-PECVD system, we firstly deposited Fe layer (about 200[nm]) on Si substrate by sputter method at the temperature of 300[℃] and hence prepared CNTs on the Fe catalyst layer and investigated fundamental properties by scanning electron microscopy (SEM) and Raman spectroscopy (RS). The optimum conditions for the CNT synthesis were found to be the gas pressure of 5[Torr], the CH_4 concentration of 20[%], the RF power of 600[W], the deposition time of 30[min], the substrate temperature of 600[℃], and the magnetic flux density of 250[G]. Furthermore, as the results of optical emission analysis, the emission intensities of CH and C_2 were very higher near the plasma periphery areas, while intensities of N_2-related emission were nearly independent of position. It can be found, from the results of SEM and RS analyses, that some carbonaceous particles and clusters were seen on CNTs when the RF power decreased below 450[W].

Acknowledgements

This research was financially supported by Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] S. Iijima and T. Ichihashi, ibid. 363 (1993) 603.
[3] D. S. Bethune, C. H. Kiang, M. S. Devries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, ibid. 363 (1993) 605.
[4] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.
[5] W.Z. Li, S.S. Xie, L.X. Qain, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[6] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fisher, R.E. Smalley, Science 273 (1996) 483.
[7] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
[8] W. Li, H. Zhang, et al., Appl. Phys. Lett. 70 (1997) 2684.

Biography

Ki-Young Jung

Ki-Young Jung was born in korea in 1983. He graduated, in 2009, from Kyungsung University, Busan, South Korea. Presently he is on a master's course at Kyungsung University, Busan, South Korea. His research interest is renewable energy and plasma applications.
Fax : (051)624-5980
E-mail: papok123@naver.com

Hyuk-Moon Kwon

Hyuk-Moon Kwon was born in korea in 1984. He graduated from Kyungsung University in 2009, Busan, Korea. Presently he is on a master's course at Kyungsung University, Busan, Korea, His research interest is renewable energy and plasma application.
Fax : (051)624-5980
E-mail : lifestyle486@nate.com

Jin-Woo Ahn

Jin-Woo Ahn was born in Busan, Korea, in 1958. He received the B.S., M.S., and Ph.D. degree in Electrical Engineering from Pusan National University, Pusan, Korea, in 1984, 1986, and 1992, respectively. He has been with Kyungsung University, Busan, Korea, as a professor in the Department of Electrical and Mechatronics Engineering since 1992. He was a visiting researcher in Speed Lab, Glasgow University, U.K., a visiting professor in the Dept. of ECE and WEMPEC, UW-Madison, USA, and a visiting professor in the Dept. of ECE, Virginia Tech from July 2006 for a year. He is director of Advance Electric Machinery and Power Electronics Center since 2005. He is also director of Smart Mechatronics Advanced Research and Training Center from Aug. 2008 and Senior Easy Life Regional Innovation System from July 2008, which are authorized by Ministry of Knowledge Economy, Korea. He is the author of five books including SRM, the author of more than 100 papers, and has several patents. His current research interests are advanced motor drive system and electric vehicle drive. Dr. Ahn received several paper awards including the Best Paper Award from Korean Institute of Electrical Engineers and The Korean Federation of Science and Technology Society in 2003, respectively. He is a senior member of Korean Institute of Electrical Engineers, a member of Korean Institute of Power Electronics and a senior member of IEEE.
Fax : (051)663-4773
E-mail : jwahn@ks.ac

Dong-Hoon Lee

Dong-Hoon Lee was born in korea in 1969. He graduated, in 1996, from Pusan National University, Busan, Korea, where he received the M. S. and Ph. D degrees, in 1998 and 2001, respectively. He joined the MIRAI project as a postdoctoral from 2001 to 2002 at the Advanced Semiconductor Research Center, the Advanced Industrial Science and Technology, Japan. He is currently an scientific review administrator of the Division of Electrical and Information Engineering at the Korea Science and Engineering Foundation (KOSEF), Daejeon, Korea. His research interest is laser engineering and application.
E-mail: dhlee@kosef.re.kr

Won-Zoo Park

Won-Zoo Park was born in korea in 1956. He graduated from Yeungnam University in 1988, Korea. He obtained his M. S. and Ph. D from Kyushu university, Japan in 1994 and 1996, respectively. Presently he is a Professor in Yeungnam University. His research interest is plasma process and application.

Youl-Moon Sung

Youl-Moon Sung was born in korea in 1966. He graduated from Pusan National University in 1992, Korea. He obtained his M. S. and Ph. D from the same university in 1994 and 1996, respectively. He undertook a post-doc. from 1997 to 1998 in Kyushu University, Japan. He became an Associate Professor in University of Miyazaki from 1999 to 2006. Presently he is an Associate Professor in Kyungsung University. His reserch interest is energy materials and application.
Tel : (051)663-4777
E-mail : ymsung@ks.ac