Chiang Mai J. Sci. 2016; 43(2) : 339-344
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Effect of Plasma Power on Copper Substrate Used for Synthesizing Carbon Nanotubes via Alcohol Catalytic Chemical Vapor Deposition (ACVD) Technique

Sureewan Phunwaree*, Wim Nhuapeng, Dheerawan Boonyawan and Wandee Thamjaree*
Department of Physics and Materials Science, Faculty of Science, Chiang Mai University,
Chiang Mai 50200, Thailand.
*Author for correspondence; e-mail: orangegii.sp@gmail.com, th_wandee@hotmail.com

Received: 15 September 2015
Accepted: 3 November 2015

ABSTRACT

In this work, the authors attempted to modify a plasma treatment on copper substrate to increase its roughness surface by Low Pressure Plasma Treatment (LPPT). Plasma energy at the radio frequency of 13.56 MHz and the mixing gas between 30% Acetylene (C_2H_2) and 70% Hydrogen (H_2) were used for treatment condition. Plasma power was varied from 90, 100 and 150 Watt for 20 min, respectively with the gas pressure of 100 mTorr were treated on copper substrate surface. After plasma treatment, treated copper substrate was then used for synthesizing carbon nanotubes via Alcohol Catalytic Chemical Vapor Deposition (ACVD) technique. The samples were then characterized using contact angle, atomic force microscopy (AFM) and scanning electron microscopy (SEM) technique, respectively. From the results, it could be seen that roughness and surface energy of copper substrate was increased with the increasing of plasma power which had affect to higher absorption of Ni catalyst and quantity of obtained nanotubes. Maximum quantity of carbon nanotubes obtained from 100 Watt for 20 min was 41.64% higher than that of non-treat sample. The average diameter of carbon nanotubes was in the range of 30-40 nm.

Keywords: Low Pressure Plasma Treatment, Alcohol Catalytic Chemical Vapor Deposition (ACVD), Carbon nanotubes

1. INTRODUCTION

In 1991, Iijima discovered multi-walled carbon nanotubes (MWNTs) for the first time, then two years later single-walled carbon nanotubes (SWNTs) was invented [1-4]. Carbon nanotubes (CNTs) is very interesting because of its special structure and properties [5-6] which exhibit extremely strong, light weight, high flexible and also showed good mechanical, electrical and thermal properties [5,7]. The structure of CNTs is a miniature cylindrical which diameter in nanoscale [1,2,8] and could be applied for many applications such as semiconductor, computing device, sensor, etc [4].

Chemical vapor deposition (CVD) is the most popular technique for synthesis CNTs [3,9] because its easily and low cost [4]. However, the diameter of MWNTs from CVD is mostly large [10]. Since diameter of CNTs depend on catalyst which deposited on substrate to apply as seeds for CNTs growth [2-3]. Therefore, there are many works have studied about the effect of catalyst on the CVD technique for CNTs synthesis. It is believed that the catalyst particles size has affect to diameter of CNTs [10-11]. So, catalyst is important parameter for synthesis CNTs and the substrate is crucial for CNTs growth [10]. Copper is requested for substrate because of its high electrical and thermal conductivity and low cost [3]. However, copper surface always have oxide layer which easy to oxidizes and crack during CVD process [3, 12-14]. Besides, it also has affect to adhesion between substrate and catalyst.

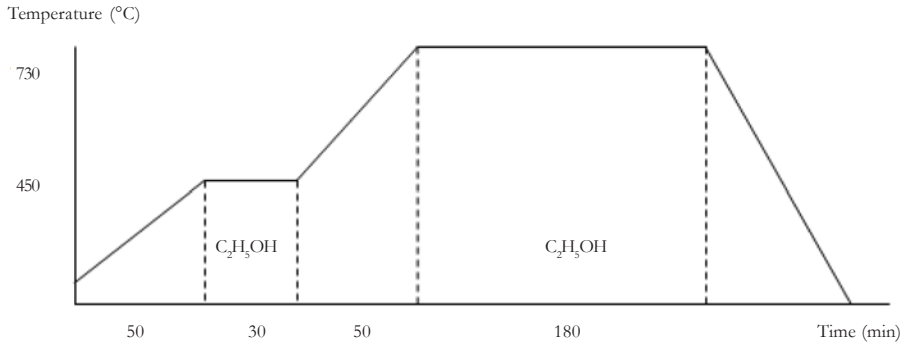


Figure 1. Temperature and time for carbon nanotubes synthesis.

Plasma technology is other alternative technique to modify surface properties of substrate. The objective of plasma treated such as cleaning, coating, printing, painting and adhesive bonding with the chemical reaction of ionized [15-17] as clean process. So that, gas of plasma is important for plasma process because it perform reaction in plasma process. Shahzad Hussain et al. [3] used radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) to improve the adhesion, growth rate and density of CNTs on copper substrate with hydrogen plasma, its reduced copper oxide of surface substrate. Hung-Chien Lin et al. [18] studied characteristic of carbon coated on optical fiber by H_2/C_2H_2 plasma. They used C_2H_2 to deposit on fiber because of its strong C≡C bond and Shinn-Shyong Tzeng et al. [19] synthesized diamond-like on silicon substrate used RF-PECVD with C_2H_2 as the carbon source. Moreover, Shuxia Wang et al. [10] studied plasma treatment with NH_3 gas plasma to the catalyst film for growth MWNTs by CVD technique and they reported that diameter and density of MWNTs changed with the plasma power and pretreatment time.

For this work, effect of plasma power on copper substrate using for synthesis CNTs via ACVD technique was studied and discussed. Surface roughness of substrate after plasma treatment was determined from contact angle measurement and atomic force microscopy (AFM), respectively. Plasma treatment effect on the growth of CNTs by ACVD technique were also investigated by scanning electron microscopy (SEM) technique.

2. MATERIALS AND METHODS

To prepare sample for plasma treatment, copper sheet with the thickness of 0.2 mm. was cut into the size of 2×2 cm^2. Sample sheet was cleaned using sonication technique with ethanol (99.5%, Merck KGaA) for 5 min and followed with acetone (99.5%, V.S.CHEM HOUSE) for 10 min. and let the sample to dry at room temperature for 10 min, respectively. For plasma treatment, Inductively Coupled Plasma Discharge (ICP), low pressure plasma technique was used in this work. Mixing gas between acetylene gas (C_2H_2) and hydrogen gas (H_2) were mixed in ratio of 30:70 and used as working gas. This plasma process was excited by radio frequency for 13.56 MHz where as plasma power was varied within 90, 100 and 150 W with the treatment time of 20 min. Moreover, plasma was run with the background pressure of 100 mTorr. After the treatment, surface roughness of the substrate was examined using Sessile drop method and atomic force microscopy (AFM) technique, respectively.

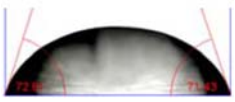
Carbon nanotubes were synthesis by alcohol catalyst chemical vapor deposition (ACVD) technique. This technique, alcohol was used as carbon source and NiO (99.8% ,SIGMA-ALDRICH,Co.) was used as metal catalyst. To prepare catalyst, NiO powder was mixed with ethanol using sonication technique for 10 min and then dropped NiO solution onto copper substrate surface to the growth of CNTs. During CNTs growth alcohol was dropped into system with the rate of 1 drop/3 seconds, temperature was heat up to 750 °C for 3 hr. Thereafter, sample was cooled down to room temperature and characterized. Morphology and diameter of nanotubes was determined using scanning electron microscopy (SEM) technique. Besides, carbon yield (%wt) was calculated and compared with quantity of nanotubes obtained from non-treatment copper substrate.

3. RESULTS AND DISCUSSION

Wettability property of non treatment and plasma treatment copper substrate was determined using Sessile drop method [11] which contact angle was measured and showed in Table 1. From the results, it could be found that the average contact angle of copper substrate were 66.21 ± 3.07, 60.27 ± 3.41 and 72.80 ± 1.90 when plasma power were 90, 100 and 150 W, respectively, whereas the contact angle of non treatment substrate was 73.08 ± 1.08.

Therefore, it could be said that plasma treatment power had affect to water absorption and could improve wettability property or hydrophilic property of copper substrate. Improvement of hydrophilic property could promote the absorption of Ni catalyst on substrate which could have affect to CNTs growth.

Table 1. Contact angle data from Sessile drop method of copper substrate.

Samples	Photo of water drop	Average contact angle (°)
Non plasma treatment		73.08 ± 1.08
90 W 20 min		66.21 ± 3.07
100 W 20 min		60.27 ± 3.41
150 W 20 min		72.80 ± 1.90

Moreover, non treatment and plasma treatment copper substrate were also characterized using AFM technique which surface roughness was measured over the

area of 10 μm × 10 μm and calculated root mean square roughness (rms). Figure 2 exhibited AFM data of copper sample which were treated and non treat plasma. It could be seen that non treatment sample exhibited slightly roughness (Figure 2. (a)) when compared with those of treated samples (Figure 2. (b) and (c)).

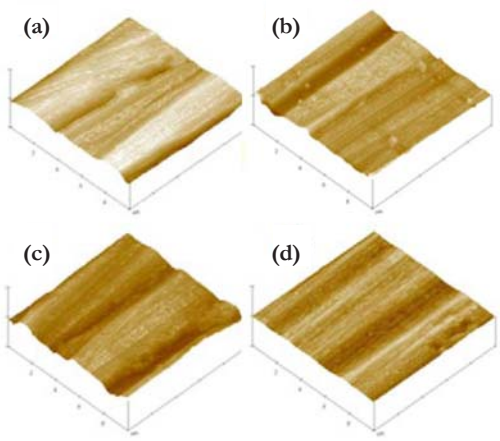


Figure 2. AFM micrographs of (a) non plasma treatment, (b) plasma of 90 W for 20 min, (c) plasma of 100 W for 20 min, and (d) plasma of 150 W for 20 min.

Therefore, it could be said that plasma treatment could improve the surface roughness of copper substrate which could be effect from the working gas in plasma treatment. For this work, it could be assumed that working gas (H_2) had reacted with oxide layer of copper substrate [11,19]. Thus, copper substrate could be cleaner and rougher after the treatment. However, copper surface seemed to be smoother when plasma power increased to 150 W. It was may be due to reaction between gas plasma and copper surface was over treatment.

Roughness value of copper substrate was shown in Figure 3. From the results, it could be seen that roughness of sample was increased when plasma power increased from 90 W to 100 W and turned to decrease when plasma power increased to 150 W. This is may be due to increased ion dissociate resulted to ion decomposition. Therefore, it could be concluded that plasma power of 100 W could promote the roughness of copper substrate which had affect to

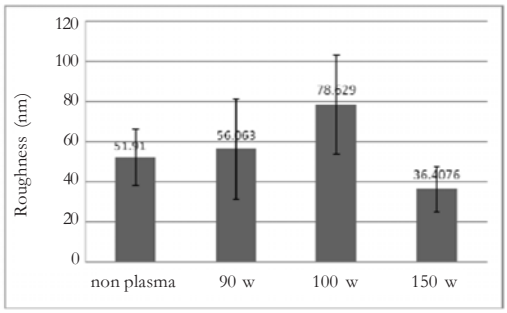


Figure 3. Roughness values of copper.

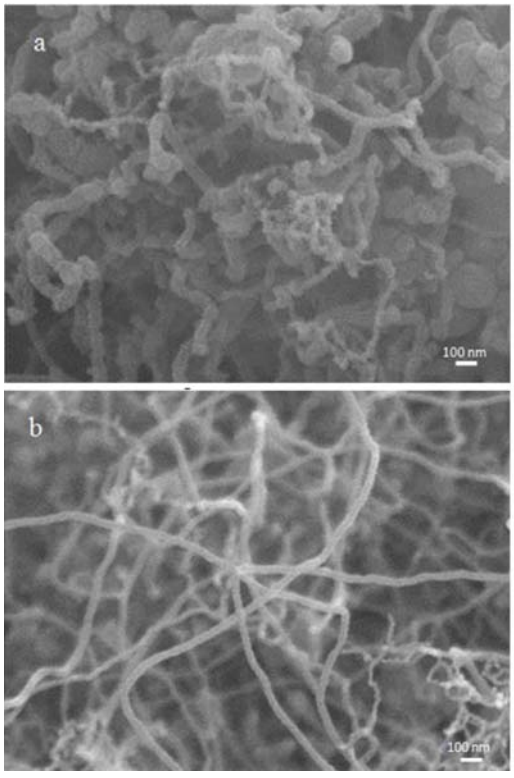


Figure 4. SEM micrographs of the CNTs (a) non treat plasma and (b) plasma treatment with plasma power 100 W for 20 min.

absorption of Ni catalyst on the substrate surface.

SEM studies (Figure 4.) were carried out to characterize the morphology of CNTs which synthesized by ACVD technique. It was observed that SEM micrographs of CNTs obtained from non treat plasma and treated plasma substrate were shown in Figure 4 (a) and (b), respectively. It could be found that characteristic of CNTs were different. Continuous long and small tubes.

CNTs could obtain from treated substrate whereas CNTs that synthesis from non treat substrate exhibited the thick tubes with nodes and agglomeration of particles which could be residual catalyst.

Diameter value of CNTs was shown in Figure 5. It could observe that the smallest diameter of CNTs could synthesis from copper substrate treated with plasma power of 100 W for 20 min and the diameters value of CNTs was 39.06 nm which 80% smaller than diameter of CNTs synthesis from non treat substrate.

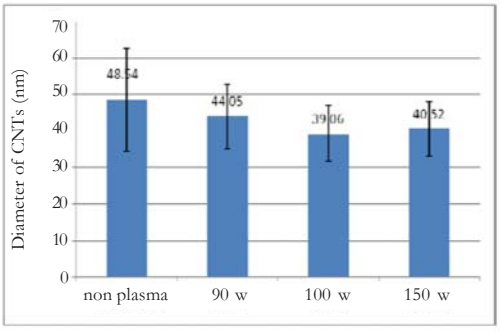


Figure 5. Diameter values of CNTs.

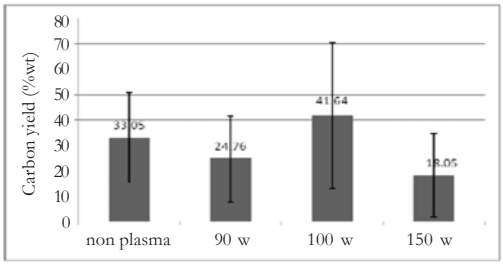


Figure 6. Carbon yield (%wt) of CNTs.

Furthermore, the carbon yield (%wt) of synthesized CNTs (Figure 6.) was also calculated using the following equation (1) [20].

$$carbon\ yield = \frac{(M_{Total} - Mc)}{Mc} \times 100\% \qquad (1)$$

where $M_{Totaland}$ is the total mass of the final catalyst and carbon products and M_c is the intial mass of catalyst. From the results, it was found that maximum carbon yield of CNTs (41.64%) was obtained from copper substrate treated with plasma power of 100 W for 20 min. However, it could be seen that carbon yield was decreased when plasma power increased to 150 W which was may be due to over plasma treatment. It could be assumed that over high power plasma had affect to less roughness and less absorption of catalyst which could be the reason of carbon yield decreasing.

4. CONCLUSION

Effect of plasma power on copper substrate using for synthesizing carbon nanotubes via ACVD technique was studied. From the results, it could be concluded that plasma power had affect to contact angle and roughness of copper substrate. Plasma power of 100 W treated for 20 min exhibited the maximum roughness of the substrate which was about 78.63 nm. CNTs were synthesis from non treat and treated plasma substrate via ACVD technique. It was found that increasing of roughness and decreasing of contact angle could improve the absorption of Ni catalyst on copper substrate which increased the carbon yield upto 41.64% (20.63% when compared with that of CNTs obtained from non treat plasma sample). Moreover, nanotubes with average diameter of 30-40 nm and less of residual catalyst also obtained from the treated copper substrate.

ACKNOWLEDGEMENT

The authors would like to thank you Thailand Graduate Institute of Science and Technology (TGIST) for financial support. And we also want to thanks the Composites and Reinforcement Nanocomposites Research Laboratory, Plasma Physic Lab CMU, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University for gratefully knowledge.

REFERENCES

[1] Iijima S., *J. Nature*., 1991; **354**: 56-58. DOI 10.1038/354056a0.

[2] Chen M., Chen C.M., Koo H.S., Chen C.F., *Diamond Relat. Mater.,* 2003; **12**: 1829-1835. DOI 10.1016/j.diamond. 2003.08.024.

[3] Hussain S., Amade R., Moreno H., Bertran E., *Diamond Relat. Mater.,* 2014; **49**: 55-61. DOI 10.1016/j.diamond. 2014.08.006.

[4] Hegemann D., Brunner H., Oehr C., *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2003; **208**: 281-286. DOI 10.1016/ S0168583X(03)00644-X.

[5] Zhang C., Xie R., Chen B., Yang J., Zhong G., Robertson J., *Carbon*, 2013; **53**: 339-345. DOI 10.1016/J.carbon.2012. 11.020.

[6] Srivastava S.K., Vankar V.D., Kumer V., *Nano-micro lett*., 2010; **2(1)**: 42-48. DOI 10.5101/nml.v2i1.p42-48.

[7] Che G., Lakshmi B.B., Martin C.R., Fisher E.R., *Chem. Master*., 1998; **10(1)**: 260-267. DOI 10.1021/cm970412f.

[8] Kumar M., Ando Y., *J. Nanosci. Nanotech*., 2010; **10**: 3739-3758. DOI 10.1166/jnn. 2010.2939.

[9] Eatemadi A., Daraee H., Karimkhanloo H., Kouhi M. and et al., *J. Nanoscale Res. Lett.,* 2014; **9(1)**: 393. DOI 10.1186/ 1556-276X-9-393.eCollection2014.

[10] Wang S., Wang P., Zhou O., *Diamond Relat. Mater.,* 2006; **15**: 361-364. DOI10.1016/ j.diamond.2005.06.036.

[11] Yun D.Y., Choi W.S., Park Y.S., Hong B., *Appl. Surf. Sci.,* 2008; **254**: 7925-7928. DOI 10.1016/j.apsusc.2008.03.170.

[12] Zhu J., Jia J., Kwong F.L., Ng D.H.L., *Carbon*, 2012; **50**: 2504-2512. DOI 10.1016/j.carbon.2012.01.073.

[13] Chaves K.L., Hess D.W., *J. Electrochem. Soc.*, 2001; **148(11)**: 640-643. DOI 10. 1149/1.1409400.

[14] O J., Lee S., Kim J.B., Lee C., *J. Korean Phys. Soc.*, 2001; **39**: 472-477. DOI 10. 3938/jkps.39.472.

[15] Taylor W., Welt B., *Technical synopsis of plasma surface treatment*, University of Florida, Gainesville, FL 2009.

[16] Dirk H., Herwig B., Christian O., *Nucl. Instrum. Methods Phys. Res., Sect. B.*, 2003; **208**: 281-286. DOI 10.1016/S0168-583X(03)00644-X.

[17] Oh J., Lee J., Lee C., *Mater. Chem. Phys.,* 20023; **73**: 227-234. DOI10.1016/ S0254-0584(10)00378-9.

[18] Lin H.C., Yu J.F., Shiue S.T., Lin H.Y., *Thin solid films.*, 2010; **518**: 7492-7496. DOI 10.1016/j.tsf.2010.05.030.

[19] Tzeng S.S., Wu Y.J., Hsu J.S., *Vacuum*., 2009; **83**: 618-621. DOI 10.1016/j. vacuum.2008.04.071.

[20] Taleshi F., *Int. Nano Lett.,* 2012; **2**: 23. DOI 10.1186/2228-5326-2-23.