**Synthesis of vertically aligned carbon nanotubes on submicron-sized dot-catalyst array
using plasma CVD method**

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Vertically aligned carbon nanotubes were synthesized on submicron-sized dot-catalyst array which have a dot size of 400 nm and dot intervals varying from 0.3 μm to 10 μm , using direct current plasma enhanced chemical vapour deposition (PECVD) method. The dot-catalyst array was fabricated by lift-off process using electron beam lithography. Field emission characteristics were measured and compared for different dot intervals. Experimental results of field emission characteristics and the Fowler-Nordheim plots suggest that spatial control of dotted-catalyst is very important to improve the electric field emission characteristics. The results show that the highest field enhancement factor β was obtained when the dot interval was two times longer than the length of CNTs.

Keyword: CNTs, dot array, plasma CVD, field emission

1. Introduction

Carbon nanotubes(CNTs) are attractive materials for many applications such as field emission display[1-3], field effect transistor[4,5] and so on, because of high aspect ratio, electrical conductivity, and mechanical strength. In particular, field emission characteristics of CNTs have been studied extensively to develop electron field emitter materials for field emission display (FED). CNTs emitters have advantages of low turn-on electric field and high current density[6-8] compared with other materials, such as diamond or diamond like carbon (DLC) film. So far, vertically aligned CNTs(VACNTs) have been widely reported using various PECVD methods on catalyst-evaporated substrate[9-13]. To achieve the aligned CNTs, electric fields of an order of $0.1\sim 1$ V/ μm were applied between the electrodes in the thermal CVD[14-16] or between the plasma sheath in the PECVD[17,18]. In the case of high density, vertically aligned CNTs, however, there remains an issue of the electric field shielding effect, which deteriorates the field emission characteristics of CNTs. Therefore, for practical applications, it is necessary to improve the field emission characteristics of CNTs by means of controlling the morphology such as diameter, density, and alignment. In other words, CNTs growth should be controlled spatially to avoid the electric shielding effect. As for the diameter control, we have proposed the use of graphene layer encapsulated catalytic metal particles for the growth of narrower multi wall CNTs (MWCNTs) using PECVD method [19]. Experimental results showed that MWCNTs grown from Ni-C composite nanoclusters have become narrower than those from Ni evaporated thin film. Their diameter was reduced from 50-100 nm to 5 nm or less. Meanwhile, there are many reports to control the CNTs density. Researchers have employed various techniques such as anodic alumina oxidation (AAO) template[20-22], photo lithography[12,23] and electron beam lithography [9,11,24-26]. Among these techniques, electron beam lithography is used generally to control the density of CNTs, which can fabricate the nano-scale patterning.

In this work, VACNTs were synthesized using DC plasma CVD method on the submicron-sized dot-catalyst array substrate which was fabricated by electron beam lithography for the purpose of developing nano-sized electron field emitters. Field emission characteristics of various samples with different dot intervals are compared and discussed.

2. Experimental details

We used the conventional thermal CVD system where a cylindrical quartz tube with an inner diameter of 40 mm and a length of 650 mm was installed inside the electric furnace. For DC plasma ignition, we inserted Titanium parallel diode type electrodes where the interelectrode distance was of about 3 mm inside the quartz tube and applied DC voltage changing from +3 kV to -3 kV to synthesize VACNTs. Samples were set near the edge of the electric furnace, where substrate temperature was 700 °C, while at the center it was 900 °C. First, pre-treatment using NH_3 gas(150 sccm) was carried out for 5 min to activate catalyst surface. After that $\text{NH}_3/\text{C}_2\text{H}_2$

gases were introduced at the pressure of 670 Pa for 5 min to synthesize the CNTs. Gas flows of NH_3 and C_2H_2 were 150 and 50 sccm, respectively.

For preparing substrates, initially chromium (Cr) was deposited on Si substrate by electron beam (EB) evaporation to form the diffusion barrier layer. After then, Fe was deposited on the substrate as catalyst. We employed the EB lithography technique to fabricate dot-arrayed catalyst substrates. After forming thin photoresist spin coating, it was exposed to EB to pattern the dot-arrayed structure on the substrate. Then Cr or Fe was deposited in turn and photoresist film was removed with acetone.

The surface morphology of CNTs were analyzed using JEOL JSM-6320F field emission type scanning electron microscope (FE-SEM). Field emission characteristics of CNTs were measured with a parallel diode configuration at a pressure of 10^{-4} Pa. A Kapton sheet with a thickness of 125 μm was used as a spacer between the electrodes.

3. Results and discussions

We have investigated the dependency of applied voltage on the morphology of VACNTs. Figure 1 shows the FE-SEM images synthesized on uniformly Fe-evaporated substrate. In the case of the positive polarity shown in Fig.1 (a), CNTs were synthesized randomly. On the other hand, VACNTs were synthesized in the case of negative polarity as shown in Fig. 1 (b), where CNTs have typical diameter of 10~30 nm and multi-walled structure. We have also confirmed that vertically aligned CNTs were synthesized only when the substrate was negatively biased with a sufficient voltage, typically higher than -2 kV. This result suggested that the electrostatic force due to the electric field in the sheath region between the plasma and substrate might play an important role to sustain the vertical growth of CNTs. The analogous phenomena on vertical growth of CNTs have been observed in the conventional thermal CVD, where the negative voltage was biased to the substrate by using parallel electrodes without any plasma discharge. From these results, it can be speculated that the Coulomb force might act on the tip of CNTs because free electrons were supplied from the substrate to the top of CNTs through interface between the CNT and Si substrate, when the substrate was negatively biased. On the contrary, when the substrate was biased positively, free electrons inside the CNTs were moved out by the electric field and there were no Coulomb force on the top because of no significant positive charges.

With the negative-biasing technique, VACNTs were synthesized on the dot catalyst array substrate, where a dot size was 400 nm, a variable dot interval ranging from 0.3 μm to 10 μm and emission area was 0.5 mm x 1.0 mm for all samples. Typical FE-SEM image of VACNTs is shown in Fig. 2, where a dot interval and length of CNTs are 4 μm and 3 μm , respectively. A typical diameter was ranging from 80 to 100 nm, which is larger compared with CNTs shown in Fig.1. This can be attributed to thicker catalyst layer compared to previous one.

We have measured the field emission characteristics of VACNTs with dot array structure to investigate the contributions of electric field shielding effect and to improve the characteristics.

Figure 3 shows the dependency of the dot interval changing from 0.3 μm to 10 μm . On-set voltages of electron emission of dot interval of 0.3, 4, 6 and 10 μm measured at an emission current of 10^{-11} A were obtained at applied voltages of about 450 V, 280 V, 140 V and 180 V, respectively. Because of the spacing of 125 μm , on-set electric fields were simply evaluated as roughly 3.6 V/ μm , 2.3 V/ μm , 1.1 V/ μm and 1.4 V/ μm , respectively. Here it is noted that CNTs of the dot interval of 6 μm show the best performance among these samples. Moreover, CNTs having the dot interval of 10 μm show the lower emission current compared to other CNTs samples. This result might be attributed to the lower number density of CNT emitters within the given observation area of 0.5 mm x 1.0 mm. Concerning to the stability of field emission performance, we have confirmed the stable continuity of emission currents for more than 2 hours.

The field emission results were analysed by Fowler-Nordheim (F-N) tunnelling theory. Figure 4 shows the F-N plot analysed using the same data of field emission characteristics shown in Fig. 3. It seems likely that the F-N plots have multiple slopes. This means that the field enhancement factor β varied depending upon the applied electric field. We are now investigating this non-linear phenomena of F-N plots in detail and these results will be discussed elsewhere. Here, we can evaluate the value of β from the extrapolated linear slopes of F-N plots, assuming that work function of CNTs is roughly 4.9 eV. We evaluated the values of β as about 480, 900, 2550 and 3380 for the dot interval of 0.3, 4, 6 and 10 μm , respectively. The turn-on voltages and field enhancement factors are summarized in Fig.5. When the dot interval is closer, β shows the relatively smaller value whereas on-set voltages were higher. These might be resulted from electric shielding effect. While the CNTs sample having the dot interval of 6 μm shows the maximum β value and minimum on-set voltage, we can expect that the electric shielding effect was weakened. Hence, the present experimental results suggested that spatial distributions on CNTs growth are very important to improve the field emission property. According to the numerical simulation of the dotted CNTs emitters having a single free-standing CNT with a length of 1 μm and a diameter of 2 nm, the highest value of electric field enhancement factor β was obtained when the dot interval was roughly two times the length of CNTs [27]. The present experimental results were consistent with the theoretical expectation, that is, β showed the highest value when the dot interval of 3 μm CNTs was roughly 6 μm . To improve the emission property furthermore, we will reduce the dot size of catalyst and diameter of CNTs in the next experiment.

4. Conclusion

In conclusion, we have fabricated the VACNTs on submicron-sized dot-catalyst array with a dot size of 400 nm and various dot intervals using DCPECVD method. The CNTs have the typical diameter of 80 -100 nm and length of about 3 μm . The effect of dot interval of VACNTs on their field emission characteristics were investigated by varying the dot interval from 0.3 μm to

10 μm . On-set voltages were significantly decreased from 450 V in the case of the dot interval of 0.3 μm to 140 V in the dot interval of 6 μm . The maximum field enhancement factor β of 3380 was obtained in the case of the dot interval of 6 μm , where dot interval was twice to the length of CNTs.

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References

- [1] W. A. de Heer, A. Chatelain, and D. Ugarte, *Science* 270 (1995) 1179.
- [2] W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park and J. M. Kim, *Appl. Phys. Lett.* 75 (1999) 3129.
- [3] Y. Saito, K. Hamaguchi, R. Mizushima, S. Uemura, T. Nagasako, J. Yotani, T. Shimojo, *Appl. Surf. Sci.* 146 (1999) 305.
- [4] S. J. Tans, A. R. M. Verschueren, and C. Dekker, *Nature* 393 (1998) 49.
- [5] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, *Appl. Phys. Lett.* 73 (1998) 2447.
- [6] W. Zhu, C. Bower, O. Zhou, G. Kochanski, S. Jin, *Appl. Phys. Lett.* 75 (1999) 873.
- [7] W. I. Milne, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, S. B. Lee, D. G. Hasko, H. Ahmed, O. Groening, P. Legagneux, L. Gangloff, J. P. Schnell, G. Pirio, D. Pribat, M. Castgnolles, A. Loiseau, V. Semet, V. T. Binh, *Diam. Relat. Mater.* 12 (2003) 422.
- [8] Y. Wei, D. Weng, Y. Yang, X. Zhang, K. Jiang, L. Liu, and S. Fan, *Appl. Phys. Lett.* 89 (2006) 063101.
- [9] Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, J. E. Calvet, J. Chen, J. F. Klemic, M. A. Reed, *Appl. Phys. Lett.* 75 (1999) 1086.
- [10] M. Chhowalla, K. B. K. Teo, C. Ducati, N. L. Rupesinghe, G. A. J., Amaratunga, A. C. Ferrari, D. Roy, J. Robertson, and W. I. Milne, *J. Appl. Phys.* 90 (2001) 5308.
- [11] V. I. Merkulov, M. A. Guillorn, D. H. Lowndes, and M. L. Simpson, *Appl. Phys. Lett.* 79 (2001) 1178.
- [12] D. H. Kim, D. S. Cho, H. S. Jang, C. D. Kim, and H. R. Lee, *Nanotechnology* 14 (2003) 1269.
- [13] M. Hiramatsu, M. Taniguchi, H. Nagao, Y. Ando, and M. Hori, *Jpn. J. Appl. Phys.* 44 (2005) 1150.
- [14] Y. Zhang, A. Chang, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, H. Dai, *Appl. Phys. Lett.* 79 (2001) 3155.
- [15] A. Ural, Y. Li, H. Dai, *Appl. Phys. Lett.* 81 (2002) 3464
- [16] H. B. Peng, T. G. Ristroph, G. M. Schumann, G. M. King, J. Yoon, V. Narayanamurti, J. A. Golovchenko, *Appl. Phys. Lett.* 83 (2003) 4238
- [17] C. Bower, W. Zhu, S. Jin, O. Zhou, *Appl. Phys. Lett.* 77 (2000) 830.
- [18] V. I. Merkulov, A. V. Melechko, M. A. Guillorn, D. H. Lowndes, and M. L. Simpson, *Appl. Phys. Lett.* 79 (2001) 2970.
- [19] M. Nagatsu, T. Yoshida, M. Mesko, A. Ogino, T. Matsuda, T. Tanaka, H. Tatsuoka, K. Murakami, *Carbon* 44 (2006) 3336.
- [20] J. Li, C. Papadopoulos, J. M. Xu, and M. Moskovits, *Appl. Phys. Lett.* 75 (1999) 367.
- [21] P. L. Chen, L. K. Chang, C. T. Kuo, and F. M. Pan, *Appl. Phys. Lett.* 86 (2005) 12311.
- [22] P. L. Pan, J. K. Chang, and C. T. Kuo, *Diam. Relat. Mater.* 14 (2005) 804.

- [23] W. I. Milne, K. B. K., Teo, M. Chhowalla, G. A. J., Amaratunga, J. Yuan, J. Robertson, P. Legagneux, G. Prio, K. Bouzehouane, D. Pribat, W. Bruenger, and C. Trautman, *Curr. Appl. Phys.* 1 (2001) 317.
- [24] W. I. Milne, K. B. K., Teo, G. A. J., Amaratunga, R. Lacerda, P. Legagneux, G. Pirio, V. Semet, and V. T. Binh, *Curr. Appl. Phys.* 4 (2004) 513.
- [25] K. B. K., Teo, S. B. Lee, M. Chhowalla, V. Semet, V. T. Binh, O. Groening, M. Castinolles, A. Loiseau, G. Pirio, P. Legagneux, D. Pribat, D. G. Hasko, H. Ahmed, G. A. J., Amaratunga, and W. I. Milne, *Nanotechnology* 14 (2003) 204.
- [26] C. S. Cojocaru, D. Kim, D. Pribat, and J. E. Bouree, *Thin Solid Film* 501 (2006) 227.
- [27] L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller and L. Schlapbach, *Appl. Phys. Lett.* 76 (2000) 2071.

Figure Captions

Fig.1 FE-SEM images of CNTs synthesized in the case of (a) +3 kV (a) and (b) -3 kV.

Fig. 2 FE-SEM images of VACNTs grown on the dot array having dot size of 400 nm and dot interval of 4 μm .

Fig. 3 Field emission characteristics of VACNTs with different dot intervals.

Fig. 4 Fowler-Nordheim plots of field emission data shown in Fig.3

Fig. 5 Dependence of dot interval of VACNTs on turn-on voltage and field enhancement factor

(a)

(b)

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