

# The Field Emission Properties of Density Controlled Carbon Nanotubes

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## Abstract

*We investigated a field emission property of CNTs grown on pre-treated substrates by H<sub>2</sub> plasma etching method in vacuum chamber (<10<sup>-7</sup> Torr). To improve the emission characteristics, various catalysts and buffer layers were used. The morphology and density of catalyst layer was controlled by the different plasma pre-treatment conditions, resulting in the control of the growth characteristics of CNTs.*

## Introduction

Carbon nanotubes (CNTs) have been extensively investigated in past few years because of their potentials in science and applications in many fields [1-5]. Up to now, many methods to synthesize the CNTs have been reported, which are arc discharge [6], laser vaporization [7], pyrolysis [8], plasma enhanced chemical vapor deposition (PECVD) [9]. Especially, PECVD method has been reported as a promising candidate for the synthesis of CNTs owing to its several advantages such as low temperature growth, easy scale up, vertical alignment.

To control the density and diameter of CNTs, we changed plasma etching parameters such as plasma power, pre-treatment time. It was founded that plasma etching conditions and buffer layers changed

the morphology and density of CNTs.

## Experiment

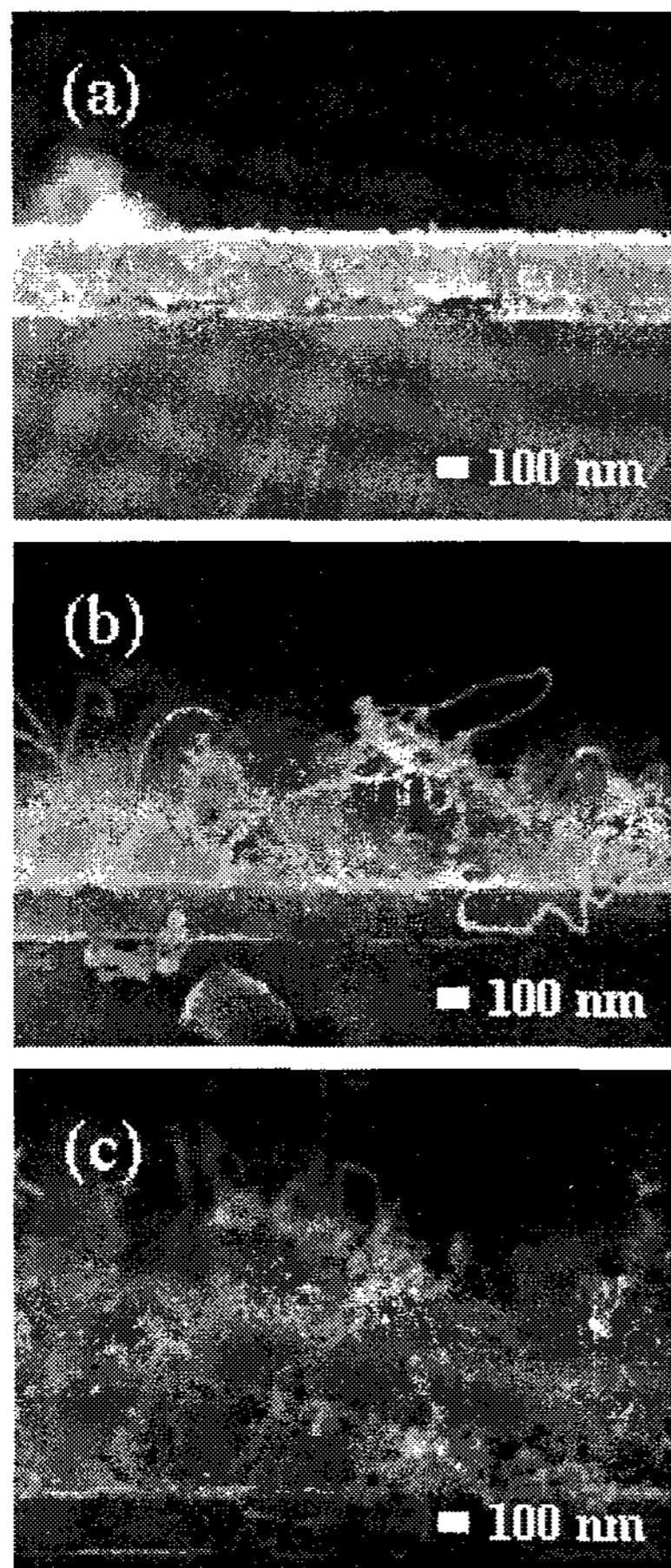
We have grown CNTs on the corning glass substrate with various catalysts and buffer layers using microwave plasma enhanced chemical vapor deposition (MPECVD). A buffer layer of 1500Å thick was coated on a glass substrate. Subsequently, various catalyst layer of 10Å in thickness was deposited by using electron beam evaporation. The CNTs were grown on different catalysts using gas mixtures of H<sub>2</sub> and CH<sub>4</sub> with given H<sub>2</sub> flow rate of 80 sccm and CH<sub>4</sub> flow rate of 10 sccm. The CNTs grown on the substrates were investigated by Field emission scanning electron microscopy (FESEM). Electron emission from CNTs was measured as a function of current density via applied voltage using a phosphor coated anode in a vacuum below 10<sup>-7</sup> Torr.

## Results and Discussion

In our previous work, we observed that plasma pre-treatment not only etched but also conglomerated the catalyst layer. Because the conglomeration effect was dominant due to the heating below a certain plasma power, catalyst film was transformed into large particles. As plasma power, pre-treatment time and thickness of catalytic layer were changed, the

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size and distribution of nanoparticles were varied [10].

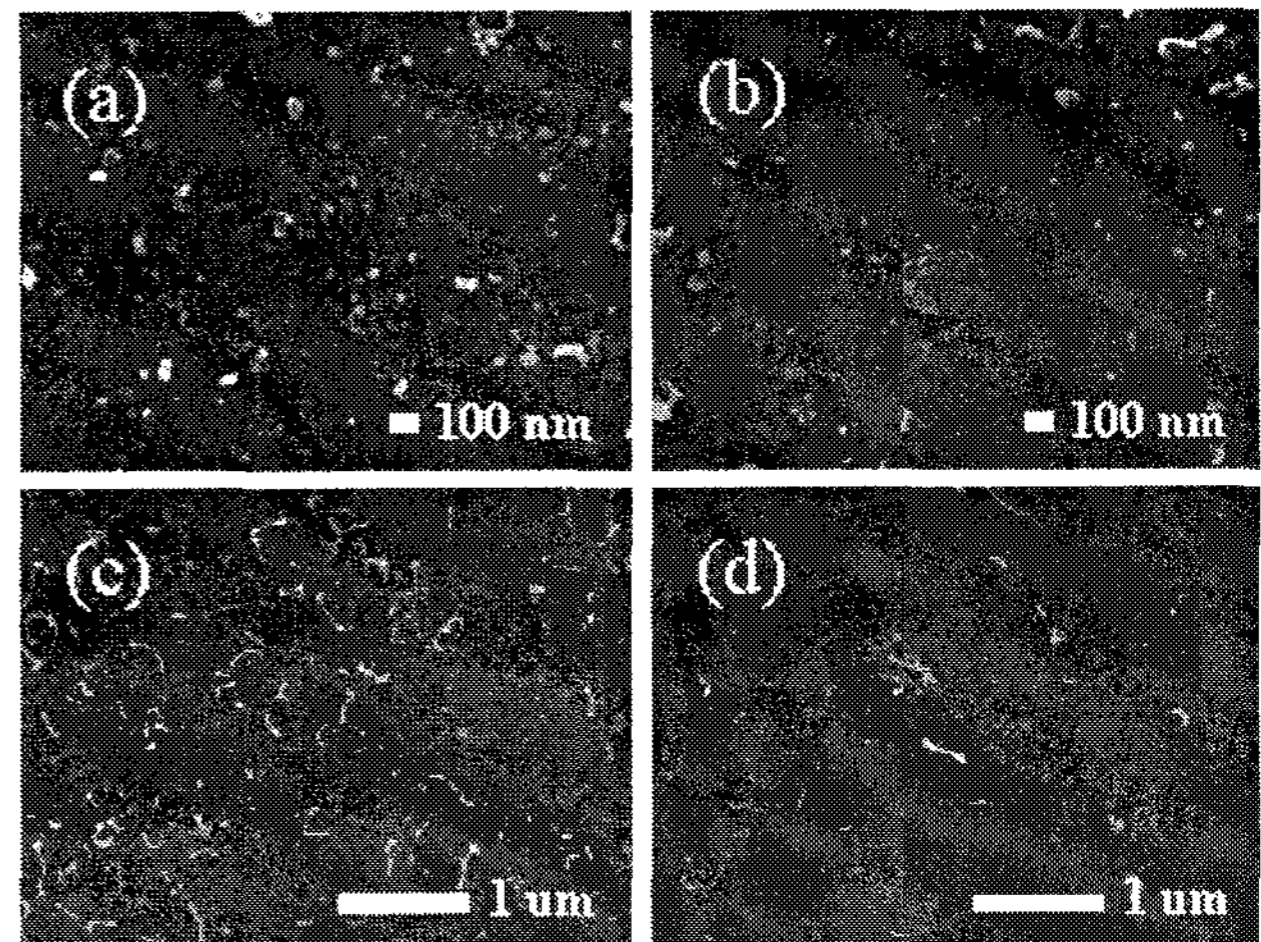


**Figure 1. FESEM images shows the cross sections of the CNTs grown on different thickness of catalyst layer: (a) 10 Å, (b) 100 Å, (c) 300 Å. All other conditions were identical.**

Fig. 1(a) shows the cross section of the CNTs grown on a Ni catalyst layer of 10 Å thick. There was no CNTs growth. But amorphous carbon was deposited on Cr buffer layer. Because the Ni catalyst layer was very thin film, the plasma of H<sub>2</sub> and CH<sub>4</sub> gas mixture etched the Ni catalyst layer before the CNTs growth started. However, the CNTs were grown on Ni catalyst layers of 100 Å thick and 300 Å (Fig. 1(b) and Fig. 1(c)). As the thickness of

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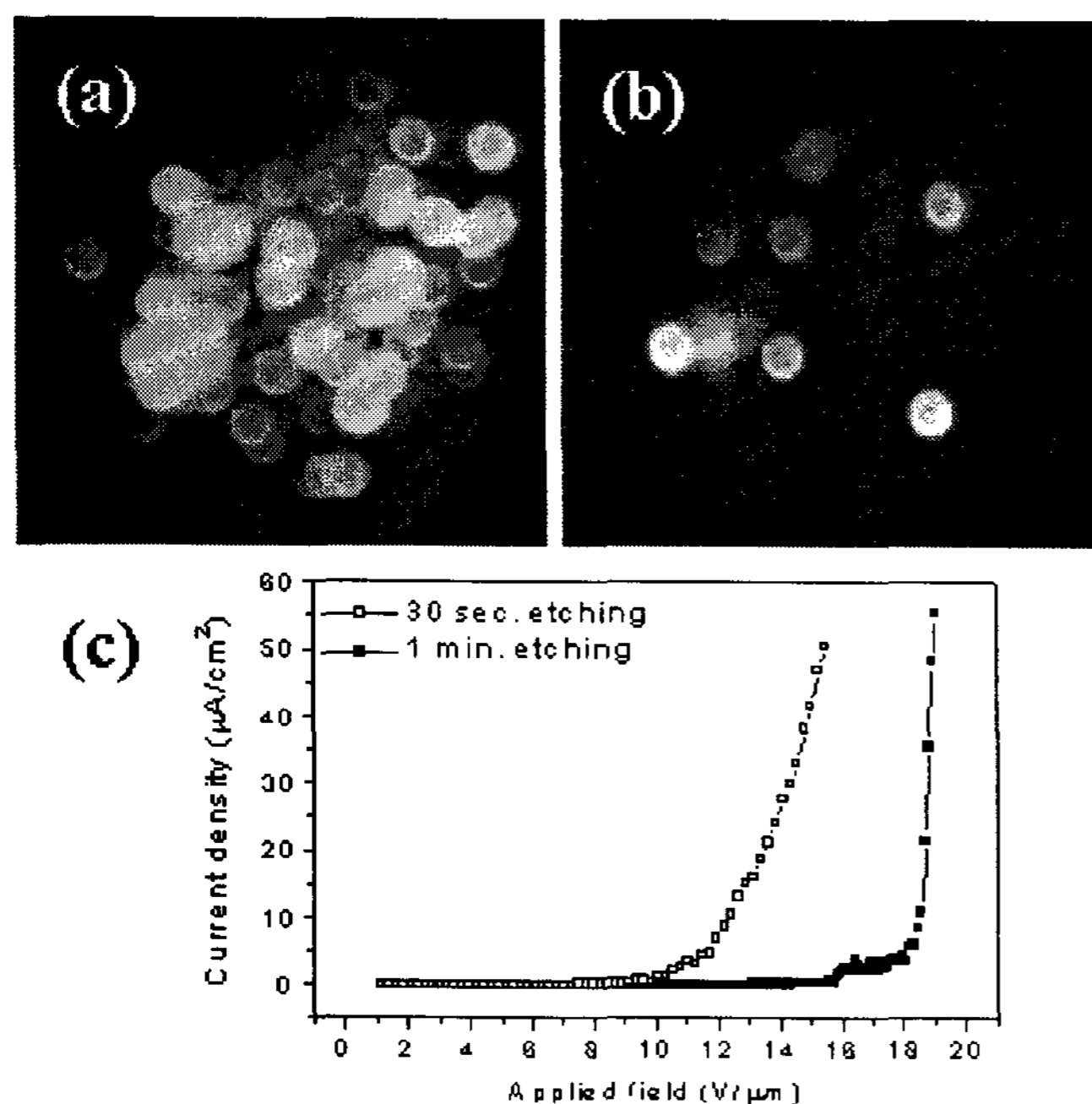
catalyst layer increased, the density of CNTs increased. In the same plasma power of CH<sub>4</sub> and H<sub>2</sub> gas mixtures, a Ni catalyst layer of 100 Å thick was more etched than a Ni catalyst layer of 300 Å thick. And has a little amount of Ni nanoparticle on surface of substrate. Thus, the density of CNTs was controlled by the thickness of catalyst layer.



**Figure 2. FESEM image shows change in the morphology of Ni catalyst layer (a), (b) and CNTs (c), (d) with H<sub>2</sub> plasma pre-treatment time.**

Fig. 2 shows the FESEM image of the morphology of the Ni film and CNTs grown on treated Ni layer with H<sub>2</sub> plasma pre-treatment time. The thickness of Ni layer was 100 Å and plasma power was 1000 W. As H<sub>2</sub> plasma pre-treatment time increased from 30 second to 1 minute, an average diameter and a density of Ni nanoparticles decreased. Subsequently, CNTs were grown on pre-treated Ni catalyst layer using a mixture of H<sub>2</sub> and CH<sub>4</sub> gas. We observed that the size of the grown CNTs was much smaller than that of the Ni nanoparticles and the density of the CNTs was not remarkably reduced (Fig. 2(c) and Fig. 2(d)). The density of CNTs also can be controlled by H<sub>2</sub> plasma pre-treatment time through

the control of the size and density of Ni nanoparticles.



**Figure 3.** Field emission images (a), (b) and current vs. applied electric field ( $I$ - $V$ ) curves with  $\text{H}_2$  plasma pre-treatment time (c).

In Fig. 3(a) and Fig. 3(b) we compare the field emission property on pre-treated samples with different densities of CNTs with the corresponding morphology seen in field emission scanning electron microscopy. We used a phosphor-coated ITO glass and applied 1500 voltage. Fig. 3(c) shows the emission current as a function of applied voltages ( $I/V$ ) of CNTs with different catalysts. The turn-on electric field,  $E_{t0}$ , was defined as the electric field at  $10 \mu\text{A}/\text{cm}^2$  of the current density.  $E_{t0}$  of CNTs with pre-treatment time for 30 second and 1 minute were 12.1 and 18.4  $\text{V}/\mu\text{m}$ , respectively.

## Conclusion

The density of CNTs was controlled by the thickness of catalyst layer and  $\text{H}_2$  plasma pre-treatment time. But the CNTs were not vertically aligned. Thus, the turn-on electric field was relatively high. We will use the  $\text{NH}_3$  and  $\text{C}_2\text{H}_2$  gas mixture for vertically aligned CNTs. The characteristics of CNTs grown on Co and Invar catalyst substrate are on studying.

## Acknowledgements

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## Reference

- [1] T. W. Ebbesen, Carbon Nanotubes: Preparation and Properties (Chemical Rubber, Boca Raton, 1997).
- [2] M. Yudasaka, R. Kikuchi, Y. Ohki, E. Ota, and S. Yoshimura, Appl. Phys. Lett. 70, 1817 (1997).
- [3] W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, Science 274, 1701 (1996).
- [4] C. Nutsenadel, A. Zuttel, D. Chartouni, and L. Schlapbach, Electrochem. Solid State Lett. 2 (1999) 30.
- [5] J.-M. Bonard, J.P. Salvetat, T. Stockli, W.A. de Heer, L. Forro, and A. Chaterlain, Appl. Phys. Lett. 73 (1999) 918.
- [6] T.S. Iijima and T. Ichihashi, Nature (London) 363 (1993) 603.
- [7] A.A. Puretzky, D.B. Geohegan, X. Fan, and S.J. Pennycook, Appl. Phys. Lett. 76 (2000) 182.
- [8] M. Terrones, N. Grobert, J. Olivers, J.P.

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- Zhang, H. Terrones, K. Kordatos, W. K. Hsu, J.P. Hare, P.D. Townsend, K. Parrides, A.K. Cheetham, H.W. Kroto, and D.R.M. Walton, *Nature(London)* 388 (1997) 52.
- [9] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, and P.N. Provenico, *Science* 282 (1998) 1105.
- [10] J. H. Choi, T. Y. Lee, S. H. Choi, J. H. Han, J. B. Yoo, C. Y. Park, T. W. Jung, S. G. Yu, W. K. Yi, I. T. Han, J. M. Kim, *Diamond and Related Materials* 12 (2003) 794.