

# Field Emission with High Performance from MgO-Coated Carbon Nanotubes

Yoshikazu Nakayama<sup>1</sup>, Supriya Chakrabarti<sup>2</sup>, Lujun Pan<sup>1</sup>, Yasumoto Konishi<sup>1</sup>, and Hiroyoshi Tanaka<sup>1</sup>

<sup>1</sup>Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

<sup>2</sup>Osaka Science & Technology Center, 3-1-10 Techno-Stage, Izumi, Osaka 594-1144, Japan

## Abstract

The high performance of field emission from well-aligned carbon nanotubes has been achieved by optimizing the thickness of an MgO coating layer on the nanotubes. It has been clarified that an MgO layer as thin as 2 nm degrades the emission properties and a thicker MgO layer does not improve the properties effectively. The most stable emission as low as 9% for 8 hrs with the lowest turn-on voltage of ~116 V is obtained for the thickness of 10 nm. The 10 nm-MgO coated nanotubes also exhibit a uniform emission from the whole area of nanotubes. The theoretical calculation of the potential distribution around the emission sites supports the existence of this optimum thickness.

## Introduction

Carbon nanotubes (CNTs) have attracted considerable attention as a material for field emission devices due to their promising excellent field emission properties.[1-3] For the realization of commercialized CNT based field emission devices, the high performance of the properties such as turn-on voltage, stability and lifetime is crucial. Coating a thin layer of wide bandgap material on the CNT surface can be promising for achieving highly stable and uniform field emission.[4] Among several wide band-gap materials, MgO can be a good choice as it has a small positive electron affinity (~ 0.85 eV) and is superior for its chemical inertness and mechanical hardness. MgO is also promising for improving the field emission from CNTs due to its high secondary electron emission coefficient if an optimum thickness can be chosen.[5,6] In this work, we have studied the thickness dependence of MgO layer coated on the vertically aligned CNTs on the field emission properties and clarified the existence of its optimum thickness to improve the properties in experimentally and theoretically.

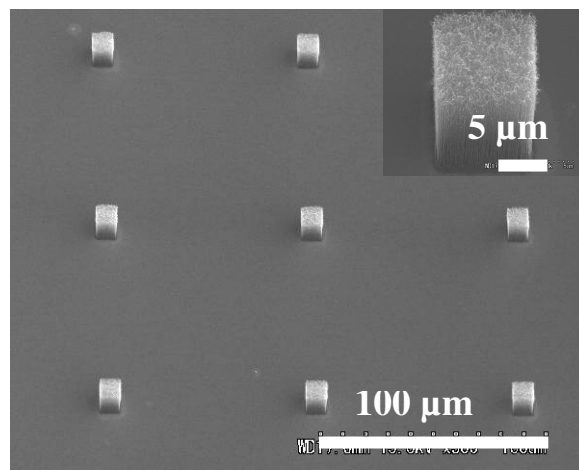
## Experiment

Multiwalled CNTs were synthesized by a catalytic chemical vapor deposition (CVD) technique. The 6 nm-thick Fe film as catalyst was deposited on an n-type (100) Si substrate and patterned with an array of 10  $\mu\text{m}$  x 10  $\mu\text{m}$  squares with the pitch of 100  $\mu\text{m}$  by a photolithographic technique. The spatially selective growth of highly aligned CNTs was performed using the patterned catalysts in the CVD chamber, where the growth temperature and time were 700°C and 120 s, respectively. The diluted C<sub>2</sub>H<sub>2</sub> with He at 13% was fed at the total flow rate of 260 sccm. The deposited aligned CNTs were then coated with MgO layers of different thicknesses of 2, 5, 10 and 20 nm at 350°C by an electron beam evaporation technique.

Microstructures of the deposited CNTs were studied by using a scanning electron microscope (SEM). The field emission measurement was carried out for the samples at a pressure of 5 x 10<sup>-6</sup> Torr in a two electrode type configuration with the gap of 150  $\mu\text{m}$ .

## Results and Discussion

Figure 1 shows the SEM images of deposited CNTs. Carbon nanotubes are grown only on the patterned catalysts and of uniform length in each zone. The length of CNTs is measured from the SEM image and found to be ~ 7  $\mu\text{m}$ . The inset shows the high magnification image, which indicates that the deposited CNTs are well-aligned in the vertical direction to the Si substrate and of high density.

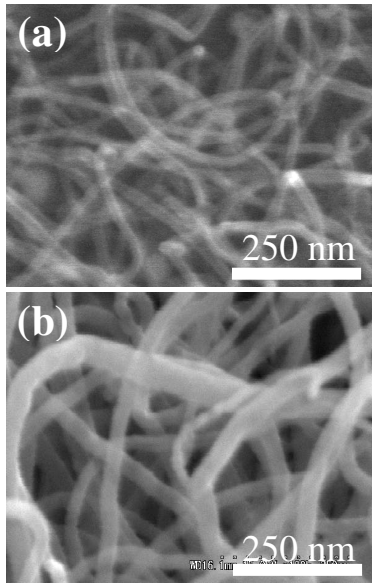


**Figure 1.** Microstructures of the aligned carbon nanotubes. The inset shows the high magnification image of one single zone.

Figures 2 (a) and (b) shows the SEM images of uncoated and 10 nm-MgO coated CNTs, respectively. The diameter of the CNTs increases from ~ 20 nm to ~ 35 nm by the MgO coating. It is also observed that the MgO coating was achieved through out the total surface of the nanotubes, not only on the tips.

Figure 3 shows the field emission current as a function of the voltage for CNTs uncoated and coated with MgO layers with various film thicknesses. Each current is the average value of three measurements from each sample. It is revealed that the 10 nm-MgO coated CNTs shows the lowest turn-on voltage of 116 V

(here defined as the applied voltage required to obtaining the emission current of  $1 \times 10^{-10}$  A).



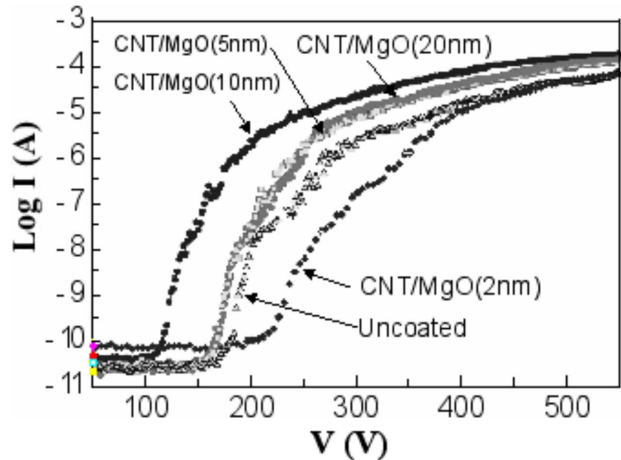
**Figure 2.** High magnification of SEM images of (a) uncoated CNTs and (b) 10 nm-MgO coated CNTs.

The field emission for a thin MgO layer (2 nm) coated sample exhibits the turn-on voltage of 200 V. This value is higher than that of uncoated CNTs which is 170 V. This result clearly indicates degradation in the field emission of CNTs when they are coated with a 2 nm-thick MgO-layer. However, 5 and 10 nm-thick MgO-layer coated CNTs show a continuous decrease in the turn-on voltage, indicating improvement in the emission property. To find out the optimum thickness of MgO coating on the CNTs, its thickness was further increased to 20 nm. However, the turn-on voltage becomes higher for the 20 nm-MgO coating than for the 10 nm-one, which indicates again degradation in the emission property. These results are in good agreement with the results reported earlier[4,7] where thicker MgO coating on the CNTs degrades the emission property. Our result has confirmed that the 10 nm-thick MgO-layer shows the best emission property from the CNTs.

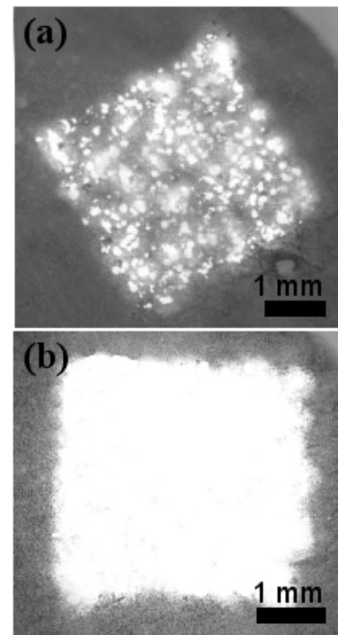
The field emission images of uncoated and 10 nm-MgO coated CNTs are shown in Figs. 4 (a) and (b). The images clearly reveal a substantial improvement in the field emission by 10 nm-MgO coating. In case of 10 nm-MgO coated CNTs almost all the zones of carbon nanotubes act as emission sites results a uniform emission, whereas for uncoated carbon CNTs many of the zones do not emit. It seems that the emission intensity is almost same at every point of the emitted region for 10 nm-MgO coated CNTs, which is important for practical application.

In order to investigate the possible explanation for the difference in the field emission property of MgO coated CNTs with different thicknesses, we have calculated the potential distribution using a finite element method.[20,21] For the calculation of the potential distribution we have adopted a model

that a vertically aligned CNT with a protruding height of 1  $\mu\text{m}$  and a diameter of 20 nm is attached on the cathode electrode. The distance between the anode and the CNT tip was 150  $\mu\text{m}$ . The applied voltage was 300 V to calculate the potential distribution of MgO coated CNTs. Figures 5 (a) and (b) show the potential distribution of CNTs with and without MgO coating. In this band diagram we have assumed the work functions of CNTs and MgO[8] are 4.5 and 4.94 eV, respectively. It is obvious that the bending of the conduction band of the MgO is different for the different thicknesses.



**Figure 3.** I-V characteristics of the field emission from aligned CNTs uncoated and coated with different thicknesses of MgO layer.



**Figure 4.** Field emission images at a voltage of 500 V from (a) uncoated CNTs and (b) 10 nm-MgO coated CNTs.

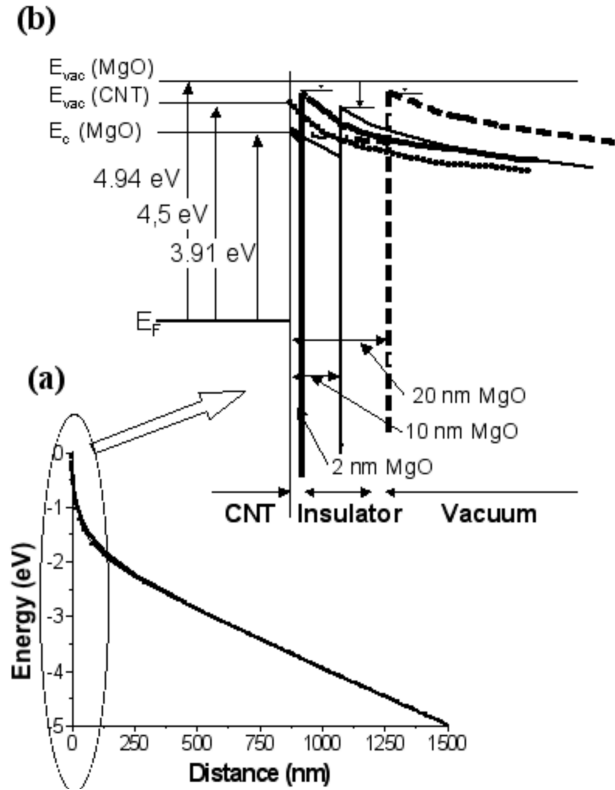


Figure 5. Potential distribution curve of MgO coated CNTs of different thicknesses and uncoated CNTs, (a) the potential distribution for long range and (b) the band diagram of MgO coated CNTs of different thicknesses including the potential distribution curves in a short range.

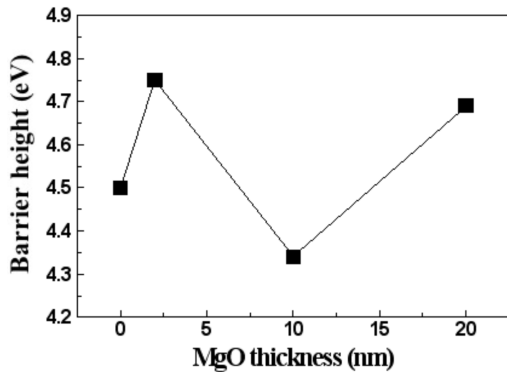


Figure 6. Plot of barrier height estimated from Fig. 5 (b) vs. MgO thickness coated on CNTs.

Figure 6 shows the barrier height as a function of the MgO thickness. For 2 nm-MgO coated CNTs the barrier height is higher than that of uncoated CNTs, which corresponds to the increase in the turn-on voltage as observed in the experiment. A significant decrease in the barrier height is obtained for 10 nm-MgO coating,

but the barrier height increases again for 20 nm- MgO coating. The change in the barrier height well explains the MgO thickness dependence of the turn-on voltage. In other words, the 10 nm-MgO coated CNTs with the minimum barrier height exhibited the minimum turn-on voltage.

It is also obvious from the figure that the slope of the band in the MgO layers is steepest for 10 nm-MgO coating. This causes the highest yield of the secondary electron emission inside the MgO layer (alpha-electron), which is associated with the highest field emission current. This is the case observed experimentally.

The stability i.e. the emission-current fluctuation with time for a fixed applied voltage was also studied for all the samples. Figure 7 shows the temporal variation of the emission current for the uncoated and MgO coated CNTs. The stability increases for 5 nm and more for 10 nm-MgO coated CNTs as compared with that of uncoated CNTs. The current fluctuation becomes minimum as low as 9% for 10 nm-MgO coated CNTs, while it is 31% for uncoated CNTs.

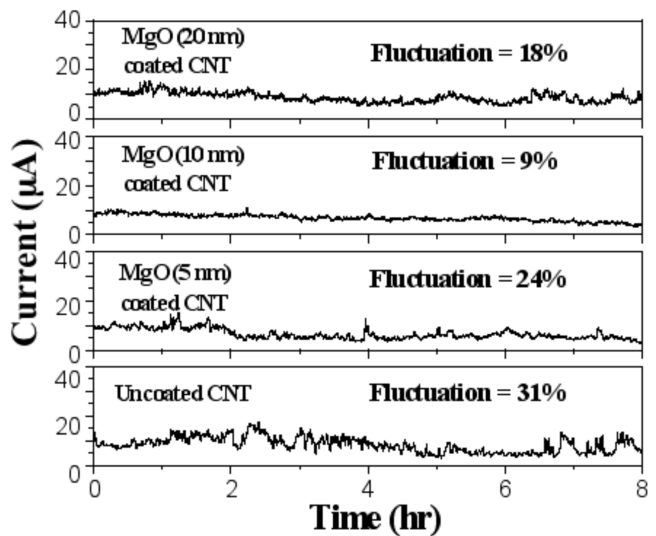


Figure 7. Temporal variation of the field emission current for CNTs uncoated and coated with MgO layers with different thicknesses.

These results indicate that the MgO coating on the CNT surface achieved the higher stability of the emission. The electron transport is diffusive in the MgO layer, by which the kinetic energy of a high-energy electron is transferred to the lattice of MgO to generate secondary electrons or alpha electrons. The coefficient of its generation is sensitive to the potential slope inside the MgO layer. The attachment and detachment of residual molecules on a CNT tip is one of the reasons for the fluctuation of field emission. For the case of MgO coated CNTs, when the emission current increases due to the attachment of a molecule, the electric resistance of the MgO layer becomes small and the potential slope inside the MgO layer becomes low. This suppresses the increase in the emission current. On the other hand, when the emission current decreases too much, the electric resistance of MgO layer becomes large to increase the potential slope inside the MgO layer. This suppresses the decrease in the emission current.

This mechanism works to stabilize the emission current. However, 2 nm-MgO layer does not work for reducing the current fluctuation. This is because electrons were transported through the MgO layer by tunneling.

## Conclusion

The clear dependence of the emission property on the thickness of the MgO layers coated on vertically aligned CNTs has been observed. The substantial improvement in the field emission property was observed when the CNTs were coated with 10 nm-thick MgO-layer. The turn-on voltage became as low as 116 V at the electrode gap of 150  $\mu\text{m}$  and the current fluctuation became only 9% whereas for uncoated CNTs the fluctuation was 31%. Low or higher thicknesses of the MgO layer, like 2 nm or 20 nm significantly degraded the emission property of the emitters. The finite element calculation of the potential at the tip of CNTs revealed that the optimum thickness of MgO effectively decreases the potential barrier for enhancing the field emission of electrons and effectively increases the potential slope inside the MgO layer for enhancing the secondary electron emission. The stability of the emission current was explained based on the consideration that the potential slope changes to keep a constant coefficient for the generation of secondary electrons.

## Acknowledgement

This work is supported by the CNT-FED project of New Energy and Technology Development Organization (NEDO).

## References

- [1] W. B. Choi, Y. H. Lee, N. S. Lee, J. H. Kang, S. H. Park, H. Y. Kim, D. S. Chung, S. M. Lee, S. Y. Chung and J. M. Kim, *Jpn. J. of Appl. Phys.* **39**, 2560 (2000).
- [2] N. L. Rupsunghe, M. Chhowalla, K. B. K. Tao and G. A. A. Amaratunga, *J. Vac. Sci. Technol. B*, **21**, 338 (2000).
- [3] J. M. Bonard, T. Stockli, O. Noury and A. Catelain, *Appl. Phys. Lett.* **78**, 2775 (2001).
- [4] S. M. Yoon, J. Chae and J. S. Suh, *Appl. Phys. Lett.*, **84**, 825 (2004).
- [5] Y. Son, S. Han and J. Ihm, *New J. of Physics*, **5**, 152.1 (2003).
- [6] V. V. Zhrinov, W. B. Choi, J. J. Cuomo and J. J. Hren, *Appl. Surf. Sci.*, **94/95**, 123 (1996).
- [7] W. Yi, T. Jeong, S. Yu, J. Heo, C. lee, J. Lee, W. Kim, J. Yoo and J. Kim, *Adv. Mat.* **14**, 1464 (2002).
- [8] J. Y. Lim, J. S. Oh, B. D. Ko, J. W. Cho, S. O. Kang, G. Cho, H. S. Uhm and E. H. Choi, *J. of Appl. Phys.*, **94**, 764 (2003).

## Author Biography

*Yoshikazu Nakayama received his B.S. in Electric Engineering from Osaka Prefecture University in 1972, and Ph.D. in Applied Physics from Osaka University in 1985. In 1972, he joined Matsushita Electric Industry Co., Ltd. In 1979, he moved to Osaka Prefecture University and has worked on solid-state physics and nanotechnology. He was appointed to the position of professor in 1995. He was also appointed to the position of eminent scholar at Osaka University in 2003.*