

P-10: Effect of Rapid Thermal Annealing on Growth and Field Emission Characteristics of Carbon Nanotubes

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Abstract

The effect of rapid thermal annealing (RTA) treatment on the growth characteristics of CNTs was investigated. We observed that Ni catalyst film was agglomerated by RTA treatment, resulting in the formation of Ni nanoparticles. The well aligned CNTs were grown from the Ni nanoparticles by plasma enhanced chemical vapor deposition (PECVD). It is shown that the size and distribution of the nanoparticles depend mainly on the annealing temperature and initial thickness of the metal layer. Also, it was found that CNTs grown through optimal RTA treatment had the more improved field emission characteristics than those of as-grown CNTs.

1. Introduction

Carbon nanotubes (CNTs) have attracted great attentions because of their unique physical properties such as high mechanical strength, thermal stability and electrical properties [1, 2]. Because CNTs have high electron emission efficiency at low voltage due to their high aspect ratio, they have been regarded as the most efficient electron emitter among various materials. Because of the shielding effect of the dense CNTs, it is necessary to control the diameter, length, and site density of CNTs for field emission [3, 4]. Although the diameter and length of aligned CNTs can be easily controlled by the thickness of catalyst layer and growth time, it is not easy to control the site density [5]. The current methods used to decrease the density of CNTs are by reducing the catalyst metal density using micro contact printing, electron-beam lithography, photolithography and shadow mask [3, 6-8]. However, the demerits of current methods are either expensive or inefficient in terms of control the site density in large area.

In this study, we used rapid thermal annealing (RTA) treatment to form Ni nanoparticles to act as catalyst for CNTs growth. We show that it is possible, by changing the metal layer thickness and RTA temperature, to alter the size and distribution of Ni nanoparticles. Also, the growth condition and field emission characteristics of CNTs were investigated.

2. Experimental

A thin layer of Ni was evaporated on the p-Si substrate with different diffusion barrier layer SiO₂ or Cr. The diffusion barrier layer prevents the formation of NiSi_x via diffusion above 300°C and maintains "active" Ni nanoparticles for the catalytic nucleation. RTA was performed to form Ni nanoparticles and the

temperature was varied from 600 to 900°C in order to find optimal temperature on the formation of Ni nanoparticles. During annealing process, Ni thin layer was found to break up into nanoparticles. After annealing process, CNTs were grown at 650°C in a mixture of acetylene and ammonia (volume ratio, 1:6) for 10 min by the PECVD. The pressure and plasma power during growth was approximately 3.25 torr and 70 W, respectively.

3. Results and discussion

In Figure 1, the evolution of the surface morphology of a series of Ni films with diffusion barrier layer SiO₂ is shown. An initial metal thickness of 10 nm was annealed for 50 sec at the annealing temperature from 600 to 900°C. The morphology of Ni film annealed at 600, 700°C shows that Ni film is still agglomerating as shown in Fig. 1(a), 1(b). As RTA temperature increased from 700 to 900°C, an average size of Ni nanoparticles increased from 120 to 180 nm as shown in Fig. 1(c), and 1(d). The results shown in Fig. 1 demonstrate that the higher annealing temperature causes to rise the formation of isolated large-size islands.

Figure 2 shows the surface morphology of two films annealed at 800°C for different annealing time with an initial Ni thickness of 10 nm. As annealing time increased from 10 to 50 sec, an average size of Ni nanoparticles increased from 100 to 120 nm.

Figure 3 shows the surface morphology of two films annealed at 800°C for 50 sec with an initial Ni thickness of (a) 5 nm and (b) 10 nm respectively. As Ni layer thickness increased from 5 to 15 nm, an average size of Ni nanoparticles increased from 45 to 200 nm. These results show that the initial thickness of the metal film can play an important role in determining surface morphology at a given temperature.

Figure 4 is SEM images of CNTs which were grown by DC-PECVD at 650°C for 15 min. Fig. 4(a) shows that the directly grown CNTs without RTA treatment have randomly oriented. But CNTs grown after RTA treatment have vertically aligned as shown in Fig. 4(b).

Figure 5 is SEM images of the Ni nanoparticles formed by RTA treatment on a 10-nm-thick Ni layer with Cr buffer layer. As RTA temperature increased from 600 to 900°C, an average diameter of Ni nanoparticles increased from 50 nm to 250 nm. Furthermore, the density and length of CNTs is remarkably reduced on the sample of RTA treatment at 600°C for 50 sec.

Finally, the field-emission properties of CNTs were characterized in vacuum of 4×10^{-6} torr. A transparent glass plate coated with

indium tin oxide (ITO) was used as anode and was separated from the CNTs layer by 80 μm . The area of ITO layer was fixed at 0.8 cm^2 . The electron emission characteristics were obtained from the CNTs in Figure 4(a), 4(b) and 6(a). As shown in Figure 7, the short and sparse CNTs have the best field emission characteristics with turn-on electric field of 2.67 $\text{V}/\mu\text{m}$.

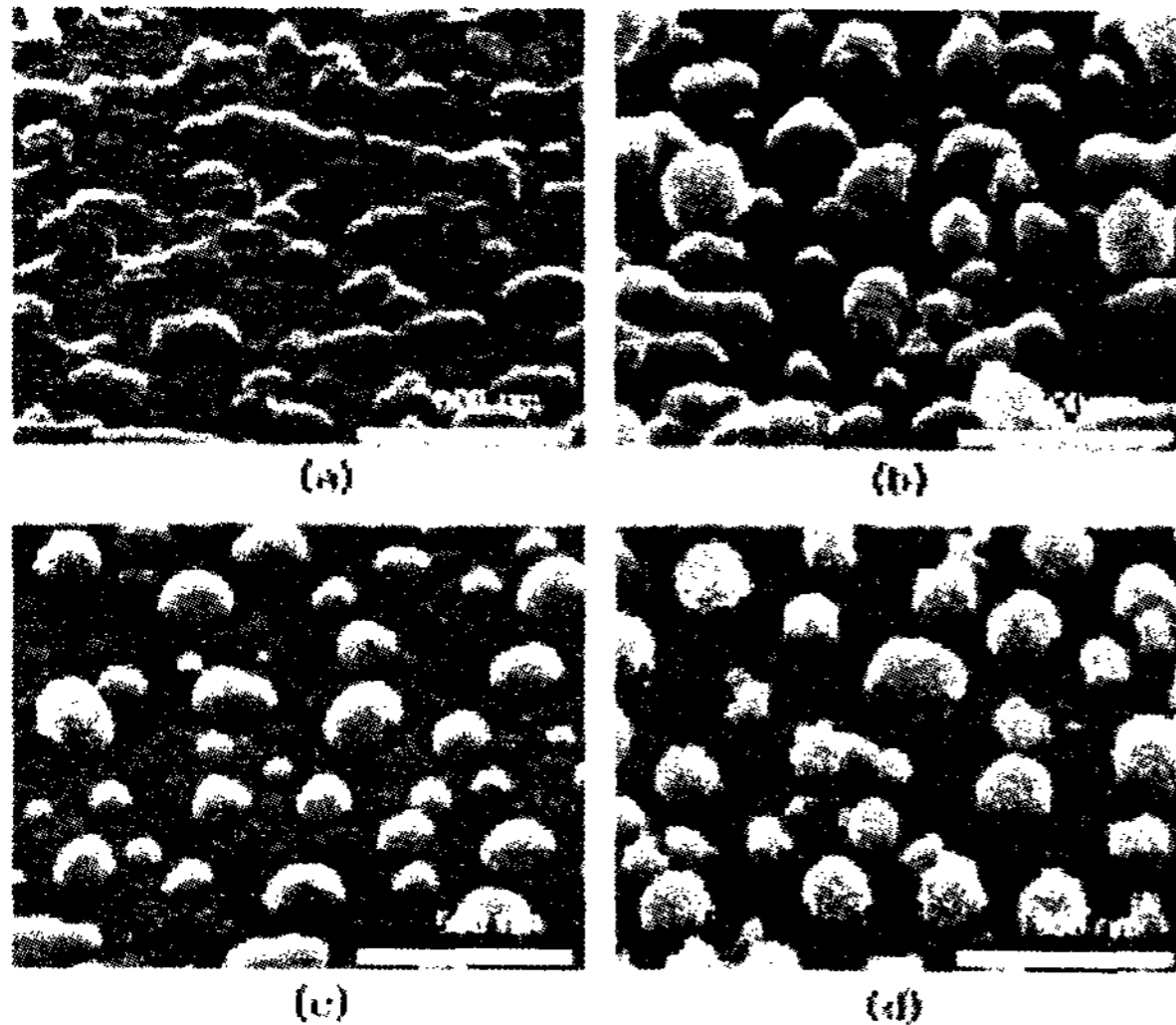


Figure 1. SEM images of the Ni nanoparticles formed by RTA treatment on a 10-nm-thick Ni layer with SiO_2 buffer layer. They were annealed at (a) 600 $^\circ\text{C}$ (b) 700 $^\circ\text{C}$ (c) 800 $^\circ\text{C}$ (d) 900 $^\circ\text{C}$ for 50 sec.

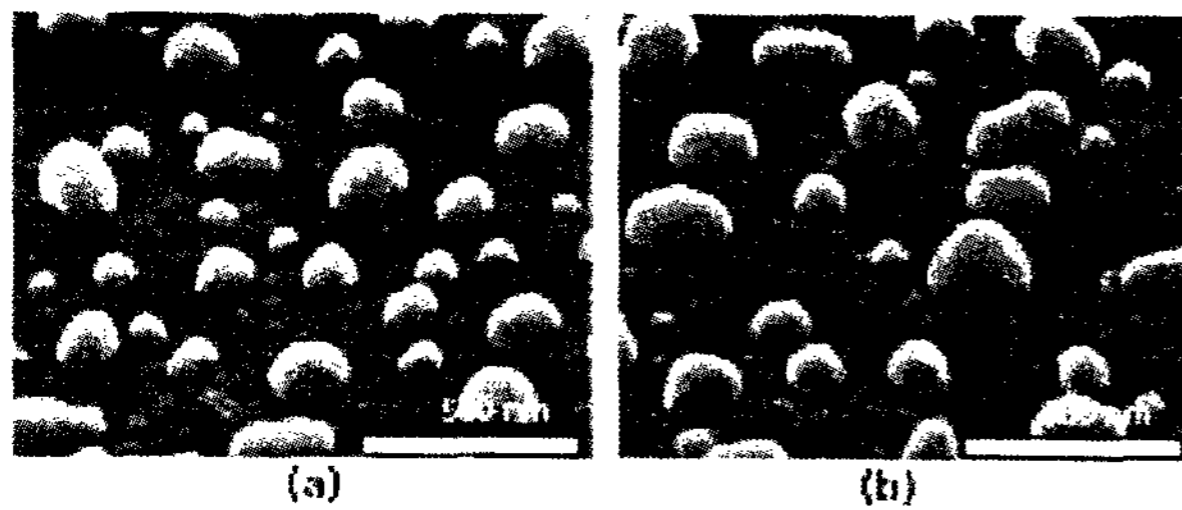


Figure 2. SEM images of the Ni nanoparticles formed by RTA treatment at 800 $^\circ\text{C}$ for (a) 10 sec (b) 50 sec on a 10-nm-thick Ni layer with with SiO_2 buffer layer.

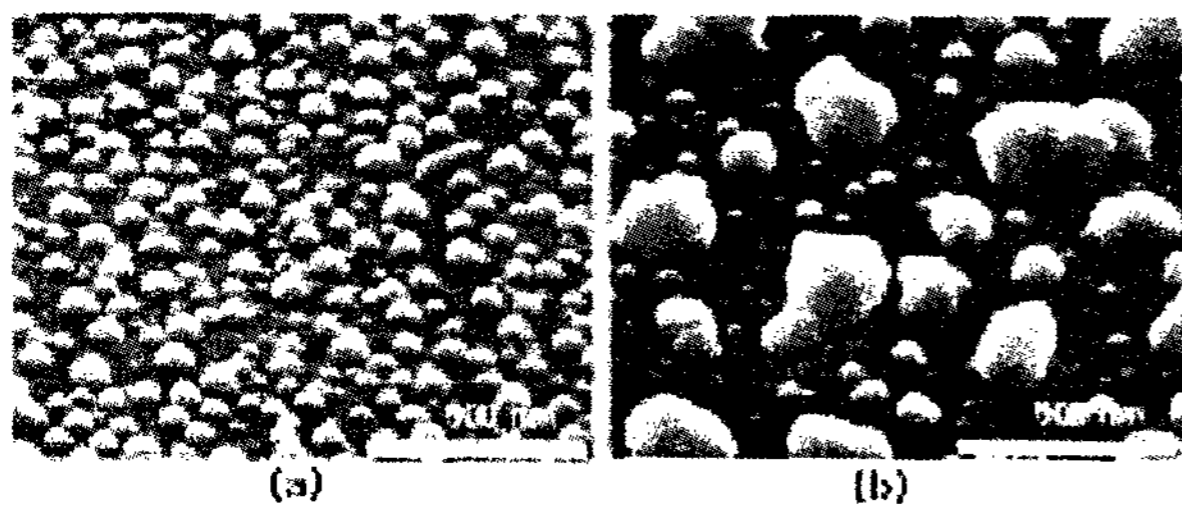


Figure 3. SEM images of the Ni nanoparticles formed by RTA treatment at 800 $^\circ\text{C}$ for 50 sec on a (a) 5-nm-thick (b) 10-nm-thick Ni layer with SiO_2 buffer layer.

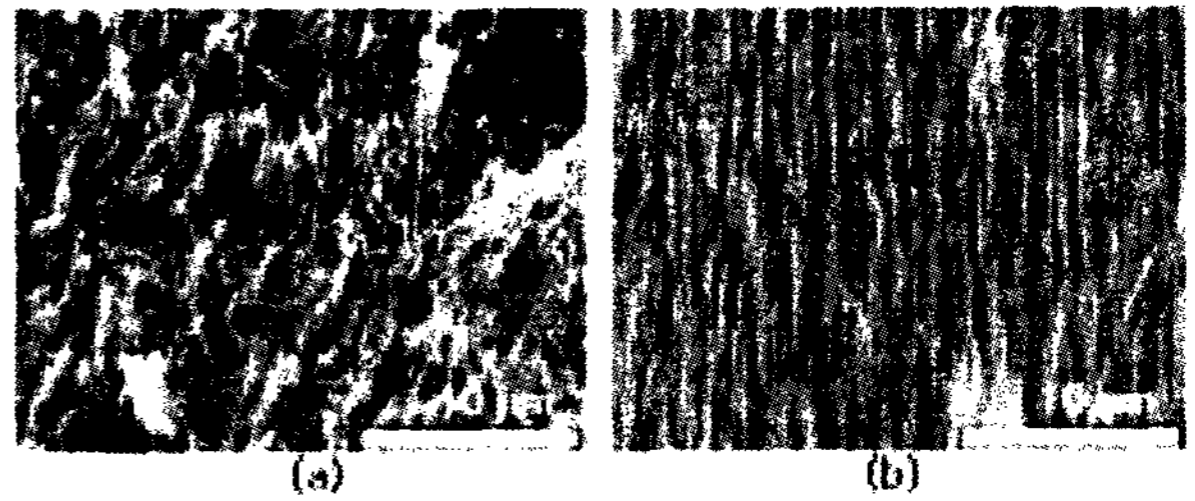


Figure 4. SEM images of CNTs grown by PECVD at 650 $^\circ\text{C}$ for the sample of (a) unannealed (b) annealed with SiO_2 buffer layer at 800 $^\circ\text{C}$ for 50sec.

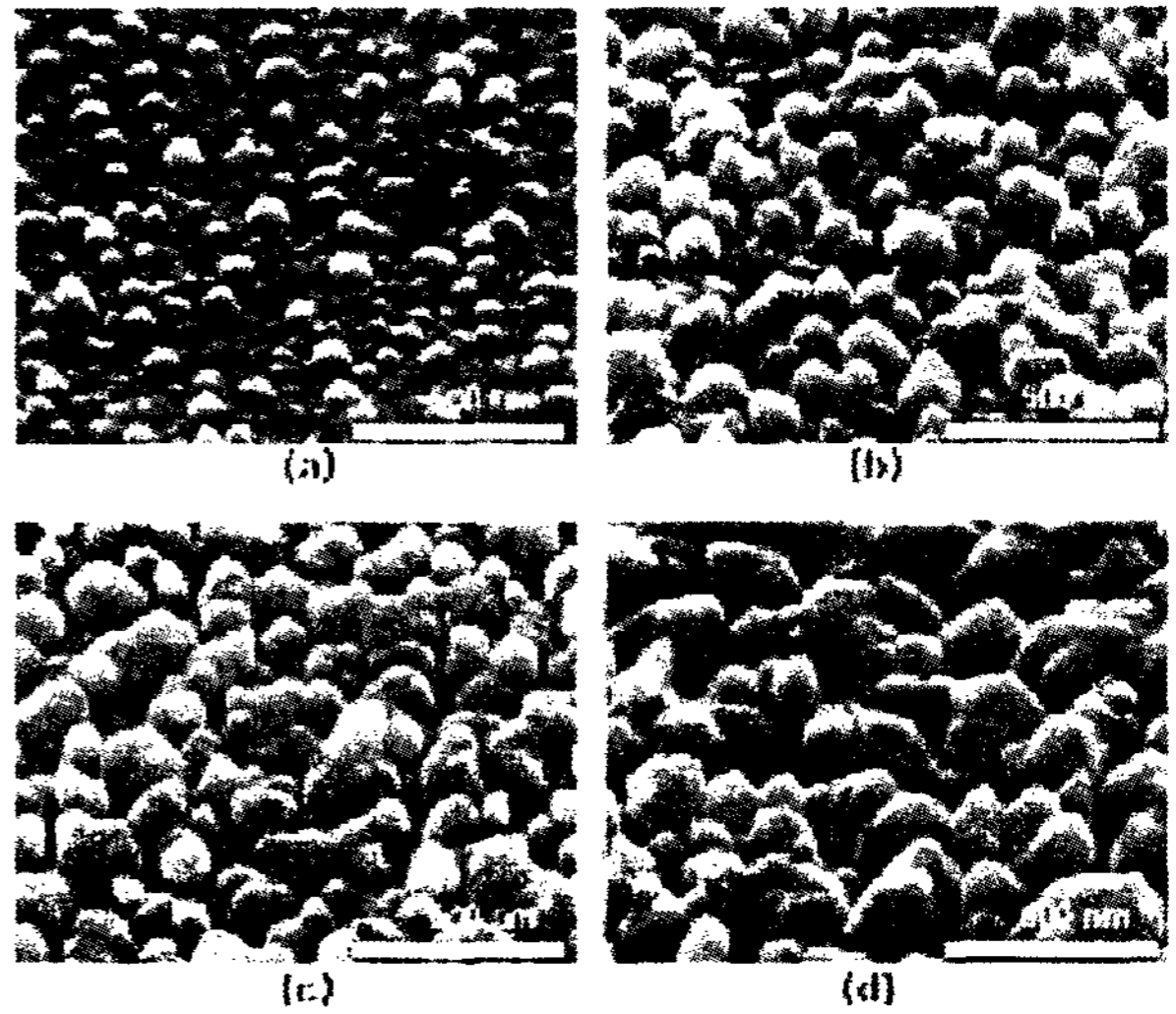


Figure 5. SEM images of the Ni nanoparticles formed by RTA treatment on a 10-nm-thick Ni layer with Cr buffer layer. They were annealed at (a) 600 $^\circ\text{C}$ (b) 700 $^\circ\text{C}$ (c) 800 $^\circ\text{C}$ (d) 900 $^\circ\text{C}$ for 50 sec.

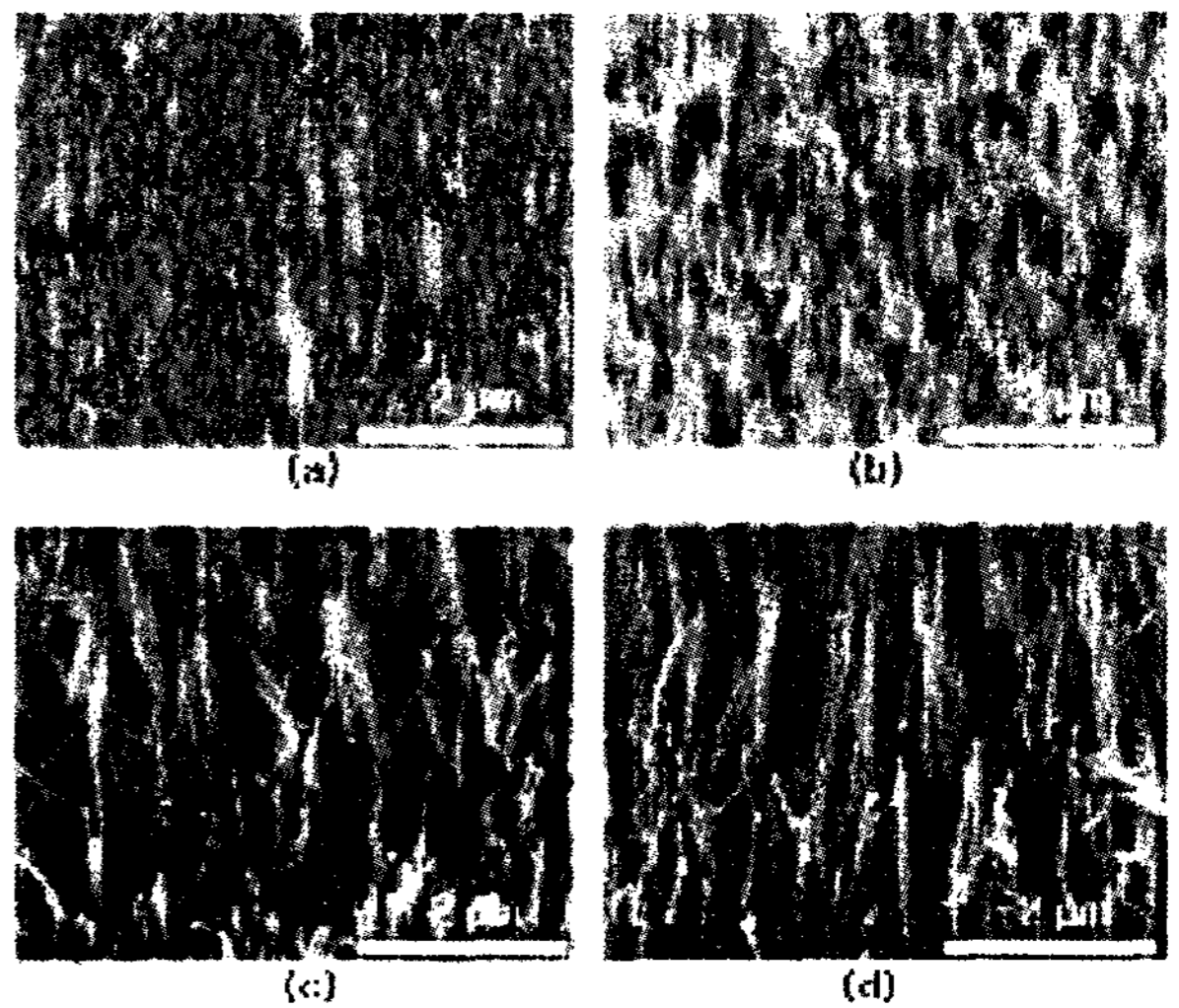


Figure 6. SEM images of CNTs grown by PECVD at 650 $^\circ\text{C}$ for the sample of Figure 5 respectively.

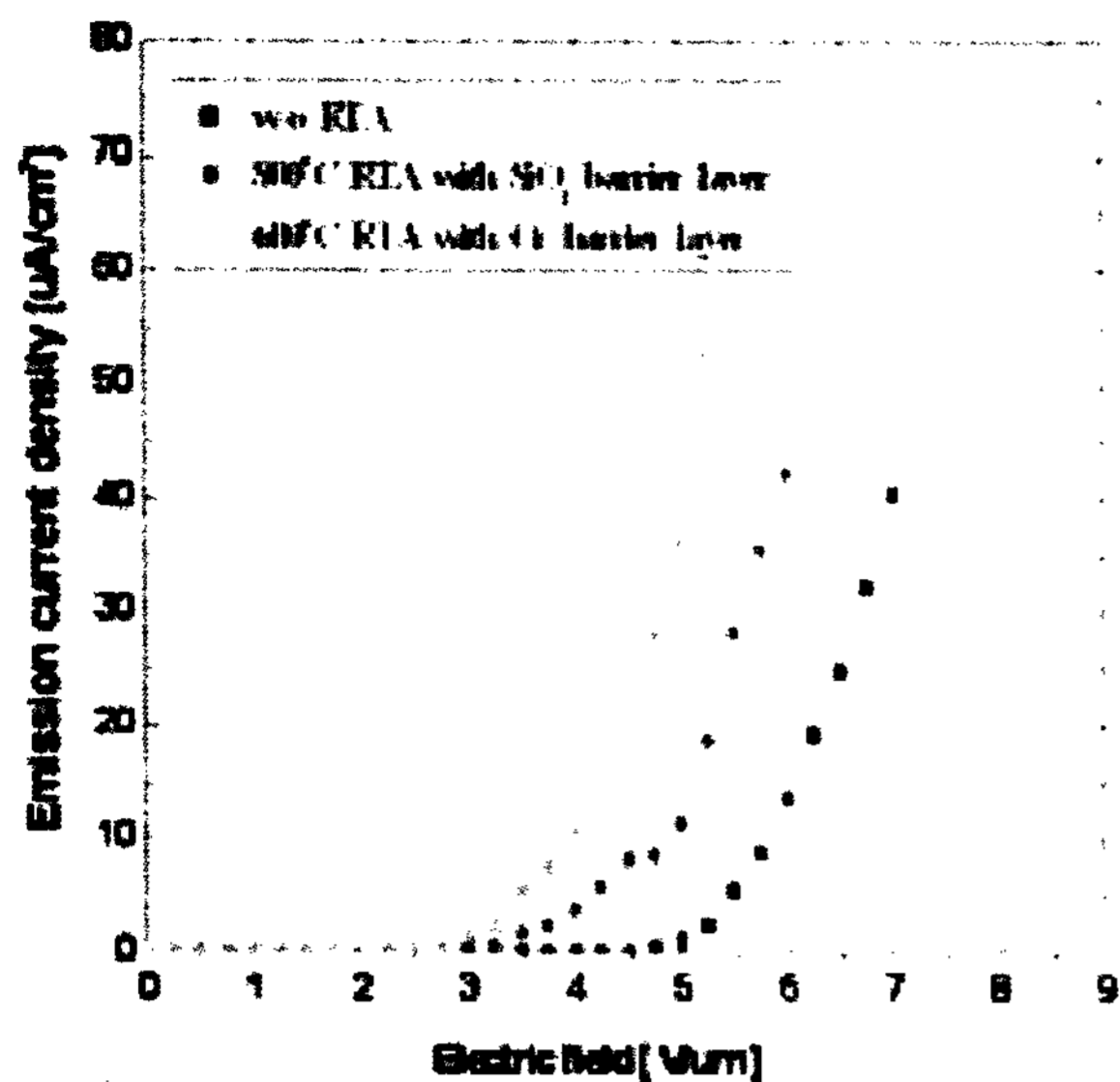


Figure 7. Comparisons of emission current density – electric field characteristics of CNTs grown with optimum RTA condition and as-grown CNTs

4. Conclusion

In conclusion, we have shown that it is possible to produce Ni nanoparticles by choosing the optimal RTA temperature, RTA time, initial Ni thickness and diffusion barrier layer. It is found that the two most crucial factors are the RTA temperature and the initial Ni thickness. And it is possible that we controlled the size and distribution of catalytic Ni nanoparticles to control the density and to obtain field emission characteristics of carbon nanotubes.

5. References

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Acknowledgement

This research was supported by a grant(M1-02-KR-01-0001-02-K18-01-016-1-1) from Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology of Korean Government.