

The Effect of Catalysts on the Growth Characteristic of Carbon Nanotubes

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Abstract

Vertically aligned carbon nanotubes (CNTs) have been produced using various type of plasma enhanced chemical vapor deposition (PECVD). Catalysts such as Ni, Co, and Fe are used for growth of CNTs. To explain the effect of catalysts on the growth characteristics of CNTs, carbon species of C₂H₂ was observed in different catalysts using optical emission spectroscopy (OES) with theoretical calculation on the surface reaction in different catalysts.

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, and compatibility with conventional Si process.

In this study, we carry out the *in-situ* analysis of chemical species for the growth of CNTs in DC-PECVD by OES. It was observed that the growth condition including various gas composition and plasma intensity affected the growth characteristics of CNTs.

Experiment

The CNTs were grown on various catalysts/Cr-coated glass substrate using DC-PECVD. A Cr layer of 1500Å thick was coated on a glass substrate. Subsequently, various catalyst layer of 300Å in thickness was deposited by using electron beam evaporation. The CNTs were grown on different catalysts using gas mixtures of NH₃ and C₂H₂ with given NH₃ flow rate of 90 sccm, 120 sccm, and 150 sccm while a constant C₂H₂ flow rate of 30 sccm. The CNTs grown on the substrates were investigated by Field emission scanning electron microscopy (FESEM). OES was used to analyze the species present in the plasma during the deposition of the CNTs. Electron emission from CNTs was measured as a function of current density via applied voltage using a phosphor coated anode in a vacuum below 10⁻⁷ Torr.

Results and Discussion

The growth characteristics of CNTs were dependent on the growth parameters such as plasma intensity, flow rate of reactant gases, and substrate temperature. The plasma condition was also changed with growth parameters. Thus, the analysis of plasma for the growth of CNTs in PECVD plays an important role in understanding of growth mechanism and process optimization.

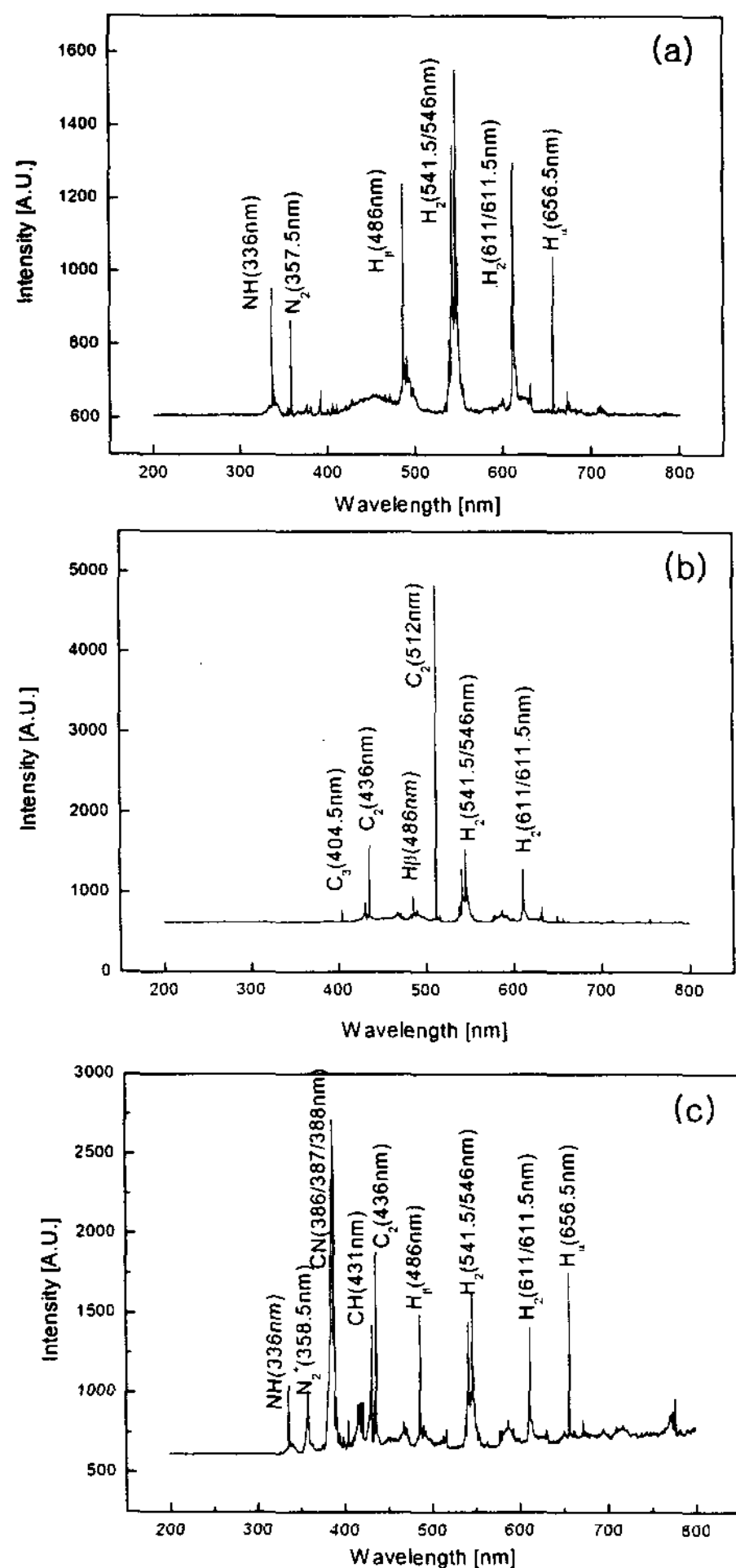


Figure 1. OES spectra detected from the plasma of NH_3 , C_2H_2 and C_2H_2 and NH_3 mixtures plasma intensity was 70 W (a) NH_3 flow rate was 120 sccm, (b) C_2H_2 flow rate was 30 sccm and (c) The flow rate of NH_3 and C_2H_2 were 120 and 30, sccm respectively.

OES spectra of NH_3 plasma shown in Fig. 1(a) reveal various radicals from the decomposition of NH_3 . However, carbon related radicals are not observed. In Fig. 1(b), the active species from C_2H_2 plasma was analyzed. Among various radicals, intensities of C_2 , H_β , and H_γ radicals were dominant [10-13]. In the plasma of C_2H_2 and NH_3 gas mixtures, spectra from the plasma of NH_3 gas and C_2H_2 gas are mixed, but N_2 radical was changed to N_2^+ radical. (Fig. 1(c))

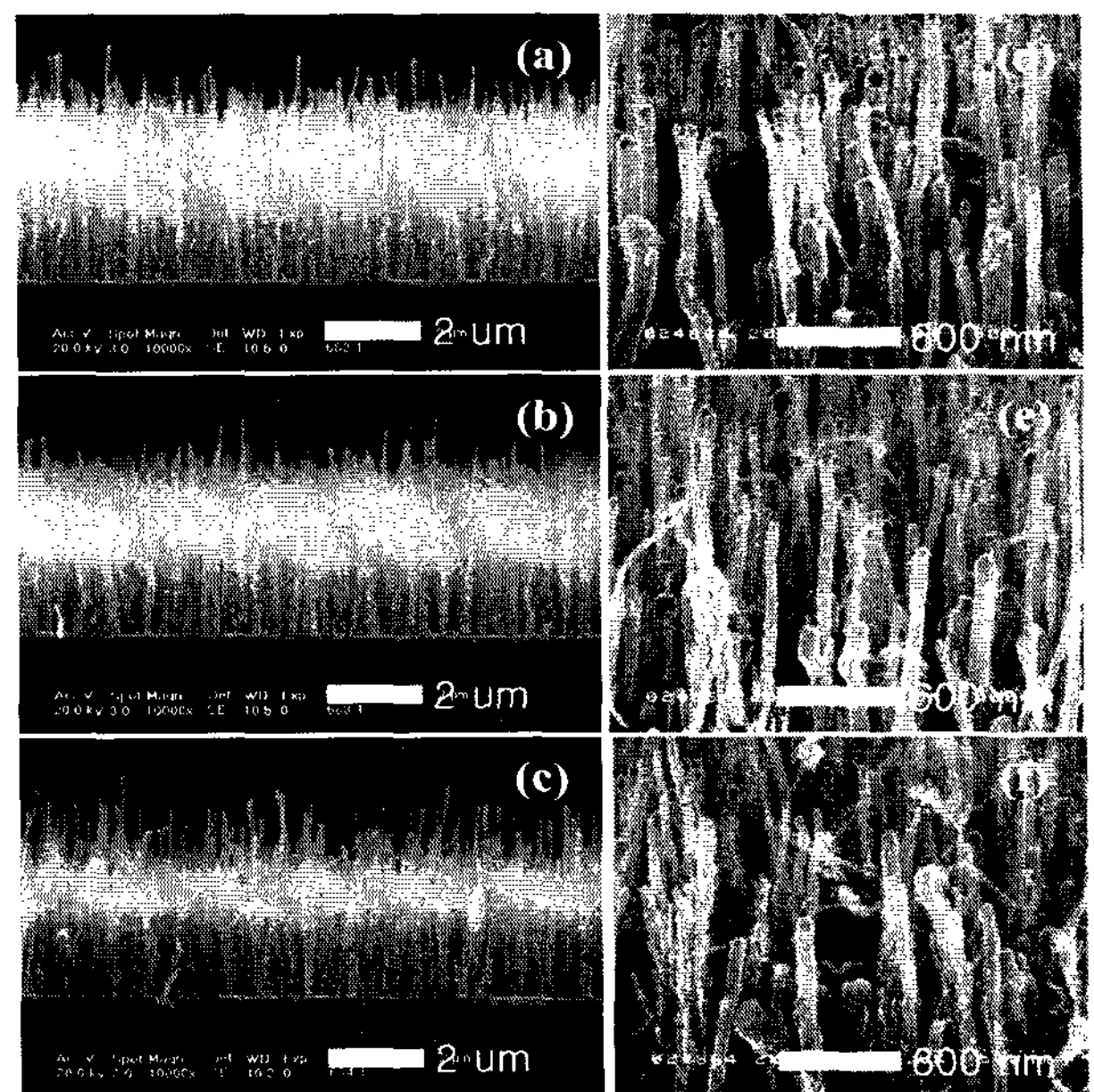


Figure 2. SEM image showing the morphology of CNTs (a) and (d) C_2H_2 (30 sccm)- NH_3 (90 sccm), (b) and (e) C_2H_2 (30 sccm)- NH_3 (120 sccm), (c) and (f) C_2H_2 (30 sccm)- NH_3 (150 sccm).

In order to study the effect of the NH_3 flow rate on the plasma condition and CNTs growth, the NH_3 flow rate increased from 90 to 150 sccm while the C_2H_2 flow rate was kept at 30 sccm. During the CNTs growth, the plasma intensity was maintained to be constant of 585 V (0.12A). Figure 2(a), 2(b) and 2(c) represents the morphology of CNTs grown on Ni coated

substrate. As the NH_3 flow rate increased, the diameter of CNTs remained almost constant but the length of CNTs decreased, indicating that NH_3 flow rate did not make an effect on the diameter of CNTs but an effect on the growth rate. Similarly, the CNTs were grown on Co coated substrate. But, as the NH_3 flow rate increased, an absorbates of CNTs surface increased. (Figure 2(d), 2(e) and 2(f))

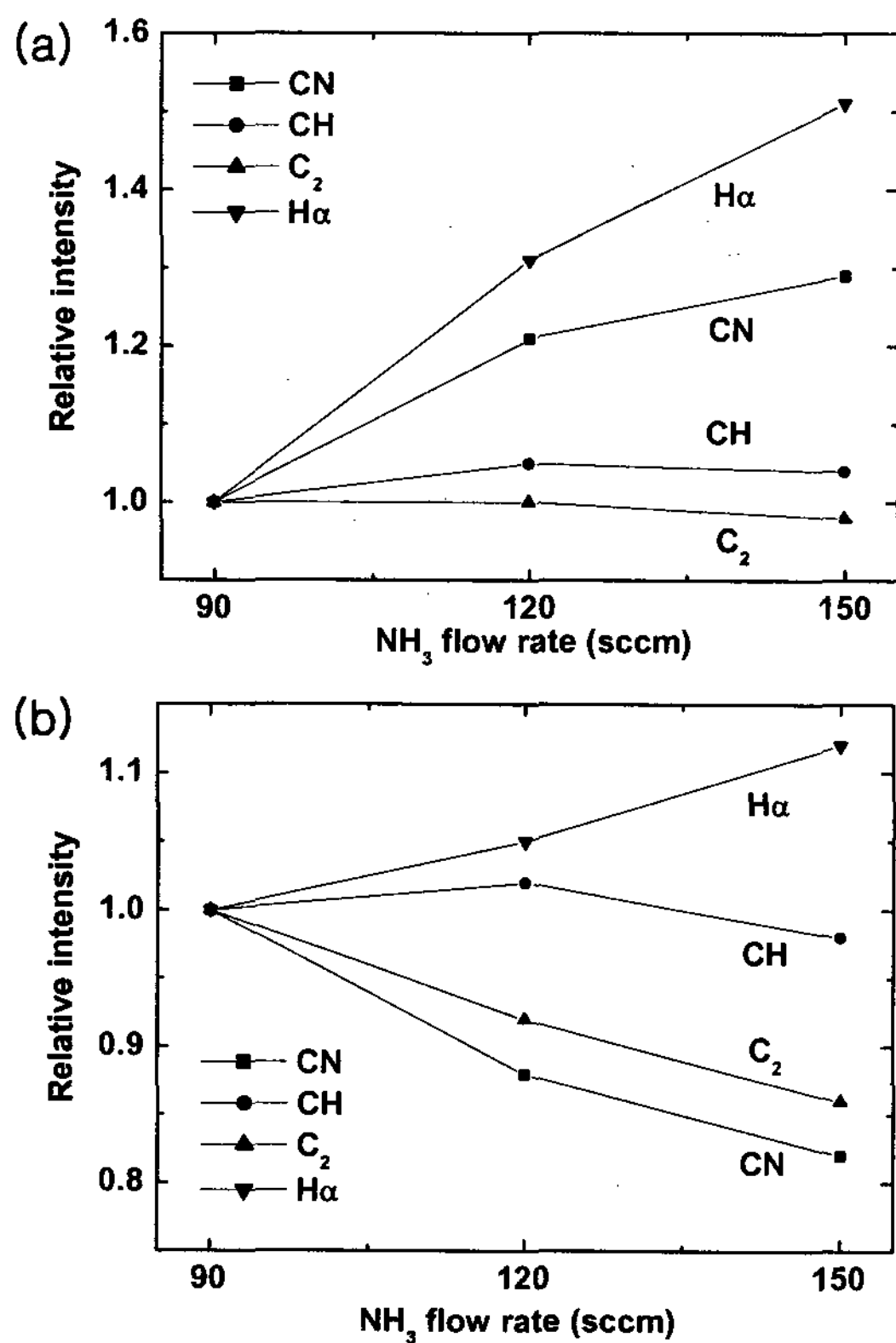


Figure 3. Relative intensities of various chemical species such as CN, CH, C_2 and H_α as a function of the NH_3 in the C_2H_2 - NH_3 plasma. (a) Ni coated substrate and (b) Co coated substrate

Figure 3 shows the relative intensities of the radicals as a function of NH_3 flow rate. In the case of Ni coated substrate (Figure 3(a)), an increase in a NH_3 flow rate enhanced the formation of hydrogen related radicals and

tightly bonded CN through overall bimolecular reactions between C_2H_2 and NH_3 . The intensity of carbon source such as CH and C_2 radical remains constant. From the dependence of relative intensity on NH_3 flow rate, NH_3 provides a hydrogen related active radicals which etch off the carbon atom on the top of catalyst metal tip during the growth of CNTs. Hydrogen related species (H_α) is considered as a main etching species. In the case of Co coated substrate (Figure 3(b)), as the NH_3 flow rate increased, the increase rate of H_α radical peak decreased, and the relative intensity of CN radical decreased. This result may be due to an increase in an amount of HCN from the formation of the atomic hydrogen and CN radical. Thus, the etching effect of H_α to remove the amorphous carbon impurities during the CNTs growth decreased, an absorbates of CNTs surface increased.

From the OES analysis on the effect of plasma intensity, the diameter of CNTs was strongly dependent on the plasma intensity through the change in catalyst nanoparticle size (not shown here) not the NH_3 flow rate.

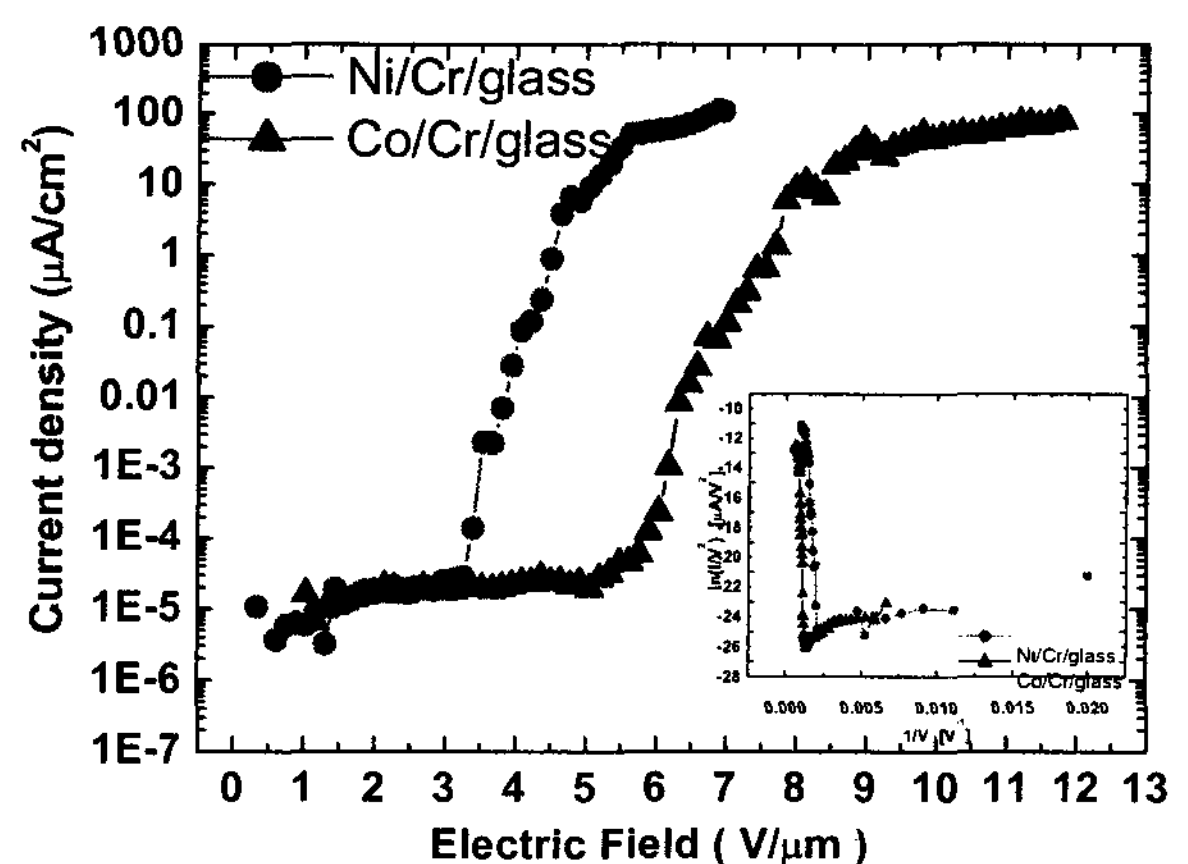


Figure 4. Current vs. applied electric field (I - V) curves with different catalyst metals.

Figure 4 shows the emission current as a function of applied voltages (I/V) of CNTs with different catalysts. The turn-on electric field, E_{to} , was defined as the electric field at $1 \mu\text{A}/\text{cm}^2$ of the current density. E_{to} of CNTs using Ni and Co catalyst were 4.5 and 7.7 $\text{V}/\mu\text{m}$, respectively.

This result may be due to CNTs grown Ni catalyst cleaner than CNTs grown Co catalyst. Thus, Ni was more efficient for the field emission of CNTs than any other catalyst metals when using the C_2H_2 gas

Conclusion

As the NH_3 flow rate increased, the diameter of CNTs remained almost constant but the length of CNTs decreased. But, in the case of Co catalyst, as the NH_3 flow rate increased, an absorbates of CNTs surface increased. Thus, Ni was more efficient for the field emission of CNTs than any other catalyst metal when using the C_2H_2 gas.

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. Puzos, D.B. Geohegan, X. Fan, and S.J. Pennycook, Appl. Phys. Lett. 76 (2000) 182.
- [8] M. Terrones, N. Grobert, J. Olivers, J.P. 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] G. Balestrino, M. Marinelli, E. Milani, A. Paoletti, I. Printer, A. Tebano, and P. Paroli, Appl. Phys. Lett. 62 (1993) 879.
- [11] T. Vandavelde, T.D. Wu, C. Quaeys, J. Vlecken, M.D. Olieslaeger, and L. Stals, Thin solid films 340 (1999) 159.
- [12] M. Okkerse, M.J.M. de Croon, C.R. Kleijn, H.E. van der Akker, and G.B. Marin, J. Appl. Phys. 84 (1998) 6387.
- [13] T. Belz, A. Bauer, J. Find, M. Gunter, D. Herein, H. Mockel, N. Pfander, H. Sauer, G. Schutze, O. Timpe, U. Wild, and R. Schlogl, Carbon 36 (1998) 731.