

The Effect of Catalysts merged with alumina on the Growing Characteristics of Carbon Nanotubes using AAO templates

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Abstract

Porous anodic aluminum oxide(AAO) templates prepared by anodizing method were used for growing multiwalled carbon nanotubes(CNTs). AAO templates with the homogeneous pore diameter and length were obtained by two step anodizing technique. Using AAO templates, vertically well-ordered two-dimensional carbon nanotube arrays were fabricated. We investigated the field emission property of CNTs grown using different catalyst metals in vacuum chamber ($<10^{-7}$ Torr) on AAO Template. To explain the different emission property, the surface reaction between catalysts and alumina pores which inserted carbon species of C_2H_2 using High resolution transmission electron microscopy (HRTEM) was studied.

Introduction

Porous anodic aluminum oxide (AAO) templates prepared by a two-step anodization process[1] have been used for the fabrication of highly ordered CNTs.[2] These nanotubes were very uniform in diameter, highly ordered, and perfectly vertical with respect to the plane

of the template. Therefore, CNTs fabricated on AAO templates are ideal substances.

Carbon nanotubes (CNTs) have been extensively investigated in past few years because of their potentials in science and applications in many fields [3-8]. Up to now, many methods to synthesize the CNTs have been reported, which are arc discharge [9], laser vaporization [10], pyrolysis [11], plasma enhanced chemical vapor deposition (PECVD) [12]. 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 have measured the field emission of CNT arrays by changing the catalysts Co, Fe, Ni. For the purpose, we study on each emission property of CNTs, grown from different catalysts. In addition, we 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/AAO using DC-PECVD. Subsequently,

various catalyst dot was deposited by using electro-chemical deposition. The method to prepare ordered AAO templates using a two-step anodization technique[1] is described elsewhere.[2] A second anodization was performed in 0.3 M oxalic acid solution at 17 °C by applying 40 V dc or in 0.3 M sulfuric acid at 0 °C by applying 25 V dc. Co, Ni, Fe was deposited in the bottom of the pores at 15 V. The CNTs were grown on different catalysts using gas mixtures of NH_3 and C_2H_2 with given NH_3 flow rate of 90 sccm, 120 sccm, and 150 sccm while a constant C_2H_2 flow rate of 30 sccm. The height of the tips that protruded was controlled by changing the etching time of the ion milled samples in a mixture of phosphoric 6 wt% and chromic acids 1.8 wt% at 60 °C. The CNTs grown on the substrates were investigated by Field emission scanning electron microscopy (FESEM) and Field emission transmission electron microscopy(HRTEM).

Results and Discussion

The catalyst nanodots, of uniform size, are well separated and exhibit an almost perfect two-dimensional (2D) array with an hexagonal pattern. For the tubes fabricated on the AAO template prepared in oxalic acid, the average tube diameter and intertube distance are 38 ± 1.0 and 104 ± 2.0 nm, respectively. The tube density is about 1.1×10^{10} tubes/cm². For sulfuric acid, they are 19 ± 1.0 and 65 ± 2.0 nm, respectively, and the tube density is about 2.7×10^{10} tubes/cm².

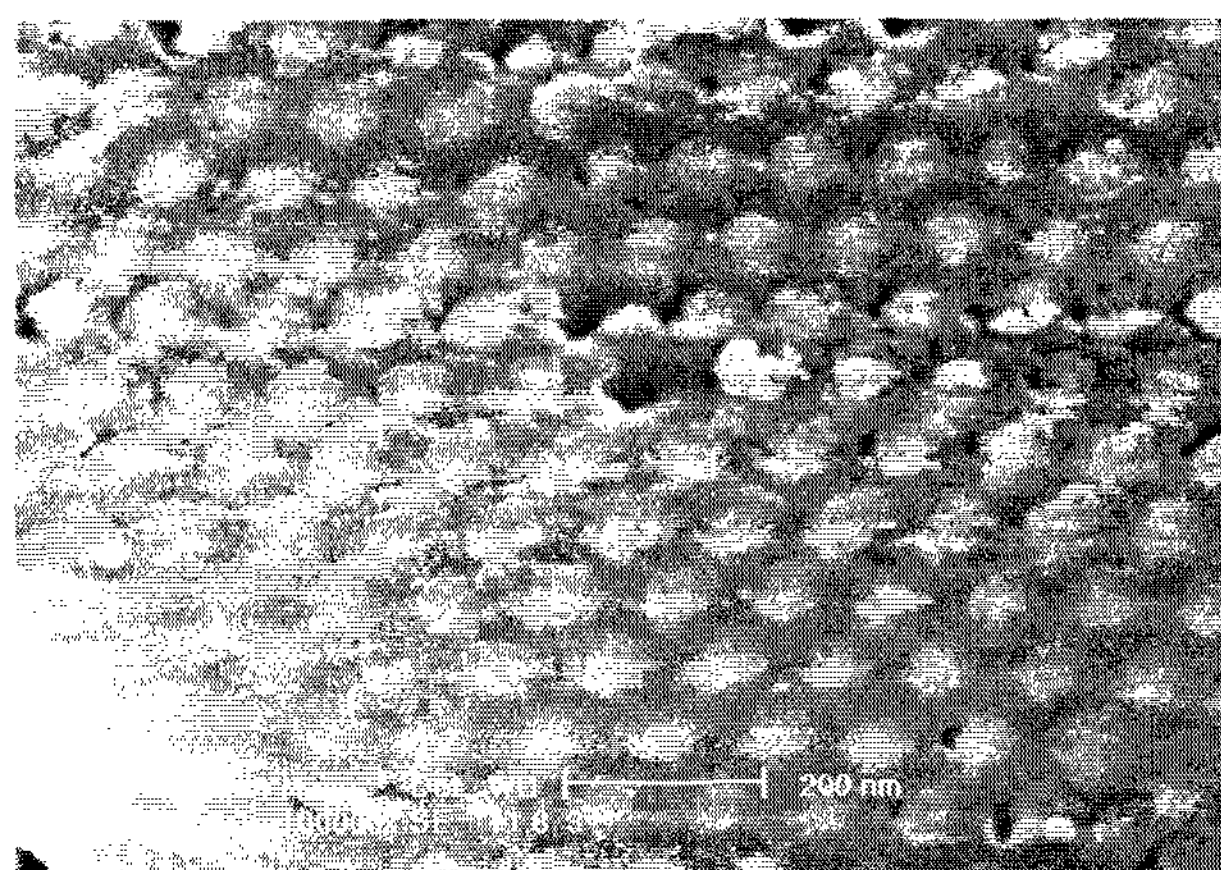


Figure 1. SEM images of Co deposited on AAO templates after ion milling.

Figure 1 shows SEM images of Co deposited on AAO templates after ion milling. 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 2. TEM image showing the morphology of CNTs (Ni Tip growth).

Figure 2 shows TEM images of CNT from

pore. But AAO is suppose to be removed during sonification in N-Butyl Alcohol for preparing TEM sample. Co particle is seen on tube tip.

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). 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. But, as the NH_3 flow rate increased, an absorbates of CNTs surface increased.



Figure 3. TEM image of CNT from Fe nanorod.

Figure 3 shows bottom growth of CNT from Fe nanorod. Other images are observed that AAO structure, Fe dot and carbon composites. It is clearly seen that tube grows out from catalyst, Fe nanorod. Moreover, alumina has amorphous structure.

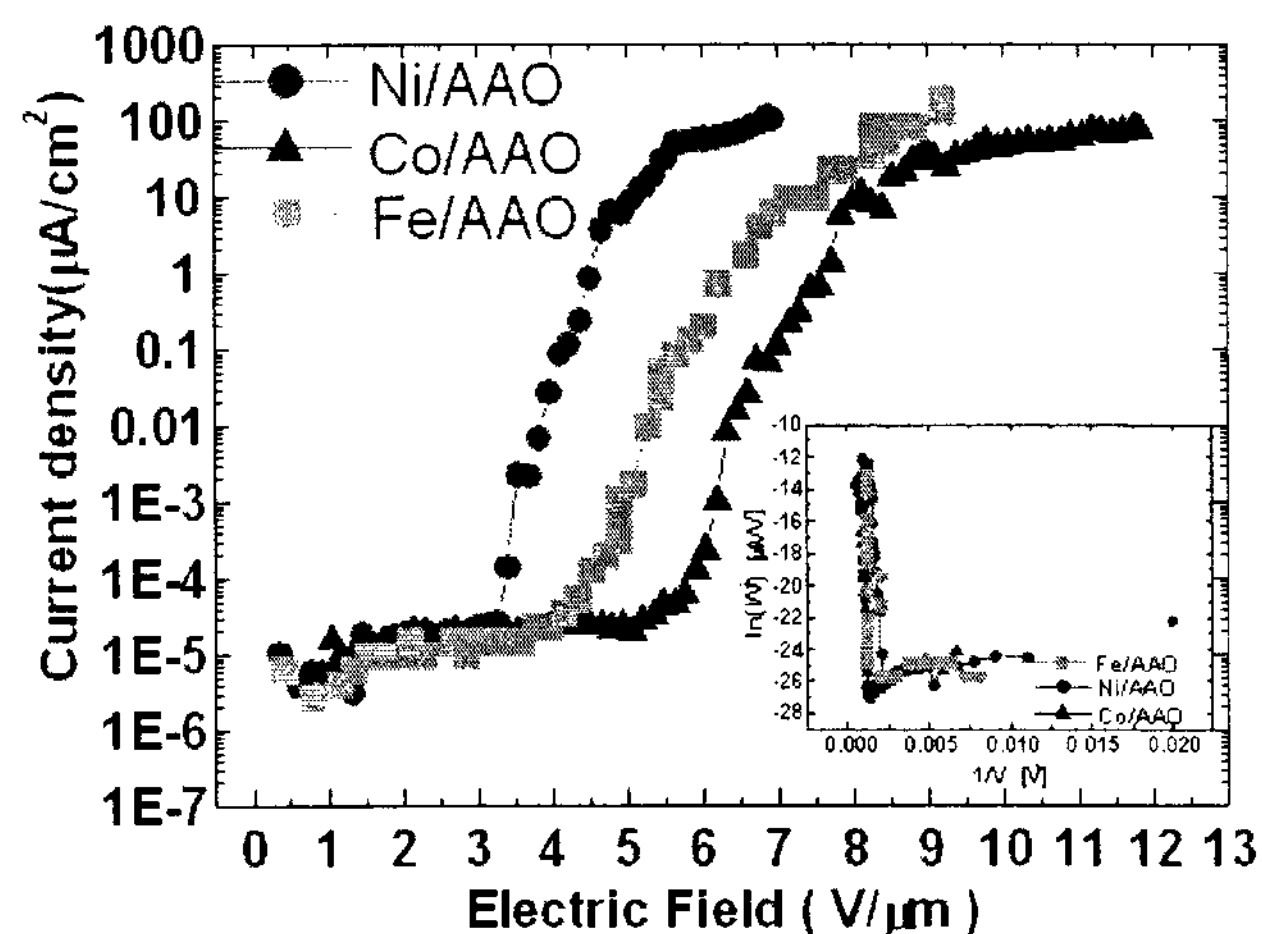


Figure 4. Current vs. applied electric field (I - V) curves with different catalyst metals.

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, Fe and Co catalyst were 4.5, 6.8 and 7.7 $\text{V}/\mu\text{m}$, respectively.

This result may be due to CNTs grown Ni was more efficient for the field emission than Co, Fe catalyst.

Conclusion

Emissions of CNTs are respectively different by changing the catalyst, Co, Ni and Fe. Additionally, 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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