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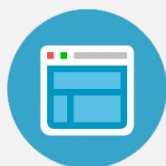
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# Effect of catalyst on growth behavior of carbon nanotube synthesizing by microwave heating thermal chemical vapor deposition process

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A modified chemical vapor deposition process, which utilizes a susceptor to absorb the microwave and to self generate the heat, for heating up the Si substrate, was used for growing carbon nanotubes (CNTs). The advantage of such a process is that the deposition chamber can be maintained at around room temperature with only the substrates localized heated, such that the deposition temperature can be more precisely controlled. The influence of the pretreatment process for catalyst-coated Si substrates on growth behavior of CNTs and the related electron field emission properties were systematically examined. Among the form of catalyst used, the  $\text{Fe}(\text{NO}_3)_3$ -ethythersilicate mixture performs much better than the dc sputtered Fe films. The higher the concentration of Fe species in the catalyst mixture, the denser the CNTs formed on the substrates, resulting in better field emission properties. Thus grown CNTs can be turned on at a very low field ( $E_0 \cong 0.78 \text{ V}/\mu\text{m}$ ), achieving a very large emission current density ( $J_e \cong 13 \text{ mA}/\text{cm}^2$ ) at  $5.5 \text{ V}/\mu\text{m}$  applied field. © 2001 American Vacuum Society. [DOI: 10.1116/1.1375818]

## I. INTRODUCTION

Since their first successful synthesis by the arc discharging technique,<sup>1</sup> and the subsequent method with the metal catalyst in an inert gas atmosphere,<sup>2,3</sup> extensive investigations on carbon nanotubes have been pursued due to their unique physical properties<sup>4,5</sup> and potential technological applications.<sup>6-8</sup> The arc discharging technique, which can synthesize the carbon nanotubes (CNTs) directly from a graphite, is simple but usually produces a mixture of carbon clusters and carbon nanotubes. The chemical vapor deposition (CVD) process can grow CNTs on a catalyst substrate and thus produced materials contain a large proportion of CNTs. The drawback in this process is that the scaling up of the process is difficult due to the high substrate temperature needed. Moreover, gas phase reaction is easily induced in such a high temperature environment.

In this article, we modified the CVD process to improve the quality of CNTs. SiC materials were used as susceptors to absorb the microwave, self generating the heat. The substrates can be raised to CNTs deposition temperature, while maintaining the surrounding at low temperature. The nucleation and growth of CNTs can be better controlled. The influence of characteristics of substrate, catalyst species, and concentration of catalyst on growth behavior of CNTs were systematically examined.

## II. EXPERIMENTS

A modified microwave enhanced plasma CVD process was utilized to synthesize the CNTs. A novel technique, which use SiC as a susceptor for absorbing the microwave to

self generate the heat, was used as a substrate heater, such that the  $\text{CH}_4$  reacts locally with catalyst coated on Si (100) substrates. The catalyst is a mixture of iron nitrate [ $\text{Fe}(\text{NO}_3)_3$ ] and ethyl-silicate [ $\text{Si}(\text{OC}_2\text{H}_5)_4$ ]. The  $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was first dissolved in ethanol with a concentration of 0.01, 0.1, or 1.0 M and then was added into ethyl-silicate drop by drop. The  $\text{Fe}(\text{NO}_3)_3$ - $\text{Si}(\text{OC}_2\text{H}_5)_4$  catalyst was then spin coated on silicone substrates, followed by pyrolysis and  $\text{H}_2$  plasma reduction processes. Pure methanol ( $\text{CH}_4$ ) with 300 sccm flow rate was used as reaction gases. The chamber pressure was maintained at about 700 Torr and substrate temperature was kept at around 1100 °C, during the growth of CNTs.

The morphology of CNTs was examined using scanning electron microscopy (Joel-800, Hitach S-4700). The electron field emission properties of CNTs coated on a Si substrate was measured using a diode setup. An indium-tin-oxide-coated glass, which served as an anode, was separated from the cathode, CNT-coated silicon, by a 180  $\mu\text{m}$  spacer. The current-voltage ( $I-V$ ) characteristics of the paralleled plates were measured using Keithley 237 under  $10^{-6}$  mbar and were analyzed using the Fowler-Nordheim (FN) model. The turn-on field ( $E_0$ ) was designated as the voltage at which the  $\ln(I/V^2)-(I/V)$  plot (FN plot) deviates from straight line. The  $\varphi/\beta$  ratio ( $\varphi_e$ ) is estimated from the slope of the straight line, where  $\varphi$  is the true work function of the CNTs and  $\beta$  is the geometric factor of the emission sites. The emission current density is estimated simply by dividing the emission current by the emitting area, which is defined by the opening of the spacer (i.e., 5 mm $\times$ 5 mm).

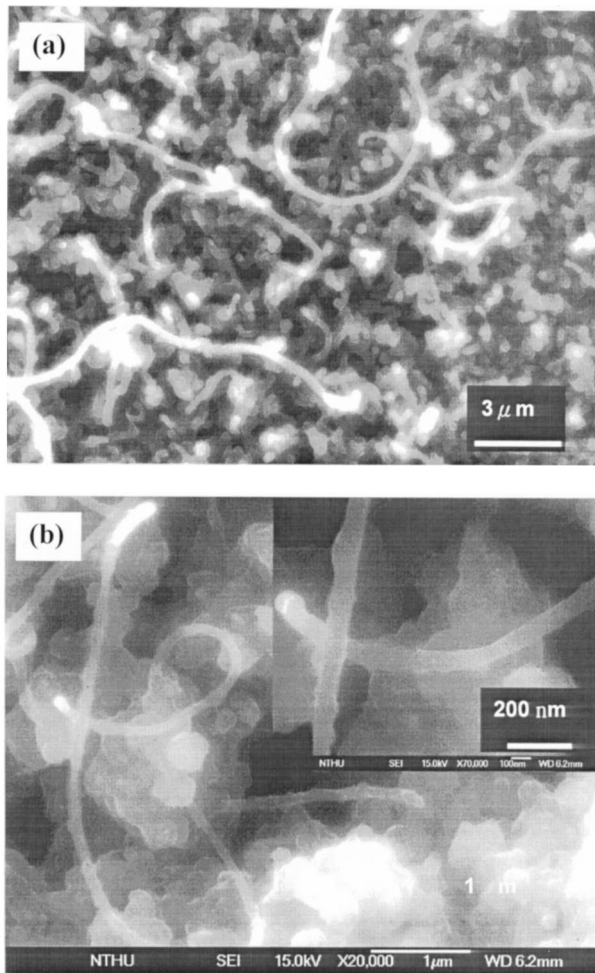


FIG. 1. Micrographs of CNTs grown on  $\text{Fe}(\text{NO}_3)_3\text{-Si}(\text{OC}_2\text{H}_5)_4$  catalyst mixture, indicating that CNTs stem out from the tip of a catalyst cluster.

### III. RESULTS AND DISCUSSION

The growth behavior for CNTs in the microwave heating thermal CVD (MHT-CVD) process is not very much different from that of the conventional CVD process. As shown in Fig. 1(a), most of the CNTs, about 300 nm in diameter, nucleate and grow from the catalysts, which are spherical Fe-containing clusters about the same size as the CNTs. Figure 1(b) and the inset illustrate even more clearly how the CNTs grow from a catalyst particle. To successfully synthesize the carbon nanotubes, the substrate temperature needs to be maintained at around 1000 °C, which is in fact the most critical conditions for the synthesis of carbon nanotubes in the MHT-CVD process. The carbon nanotubes thus obtained, which are curved and about several microns in length, distribute over the substrates uniformly, and the number density of carbon nanotubes increases with the concentration of Fe clusters contained in the catalyst mixture, as illustrated in Figs. 2(a), 2(b), and 2(c). These results clearly imply that, in the  $\text{Fe}(\text{NO}_3)_3\text{-Si}(\text{OC}_2\text{H}_5)_4$  mixture, the Fe clusters are the acting catalytic sites, promoting the formation of carbon nanotubes. The  $\text{Si}(\text{OC}_2\text{H}_5)_4$  is presumably reduced to Si clusters due to preheating under reducing atmosphere in the

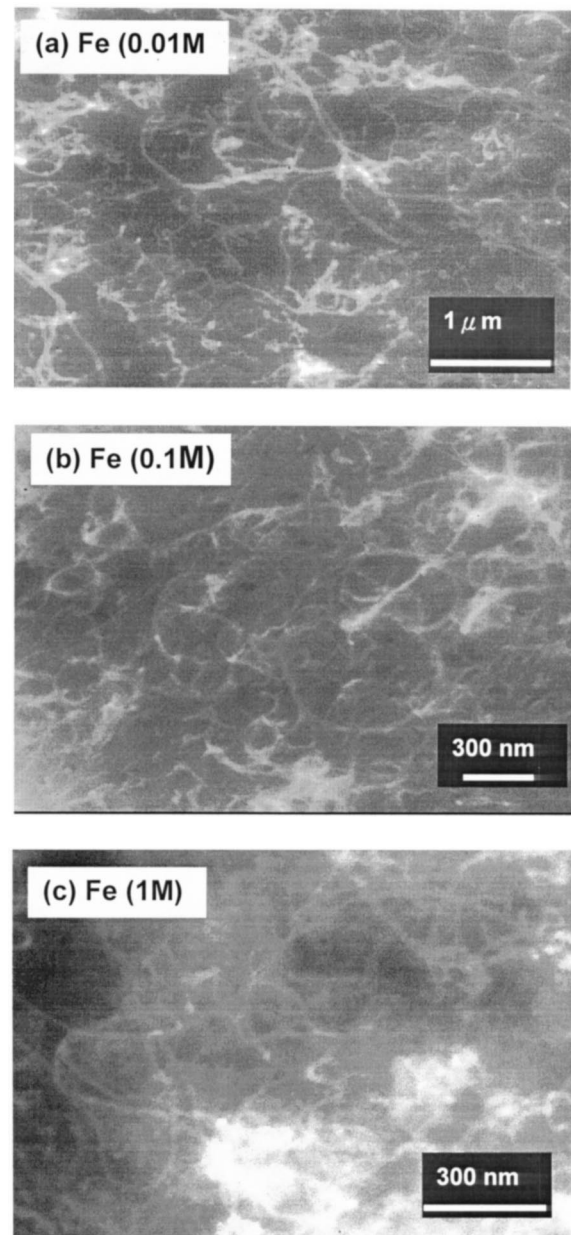


FIG. 2. Variation of morphologies of CNTs grown on  $\text{Fe}(\text{NO}_3)_3\text{-Si}(\text{OC}_2\text{H}_5)_4$  catalyst mixture with the  $\text{Fe}(\text{NO}_3)_3$  concentration in the catalyst mixture.

CVD process. The Si clusters not only react with Fe clusters, but also interact with the Si substrate, which improves the adhesion of carbon nanotubes. The CNTs to Si interaction is expected to improve the electron transport from substrates to emitting materials, CNTs, since the electron transport barrier is greatly reduced.

The electron field emission properties of the thus obtained carbon nanotubes are shown in Figs. 3(a), 3(b), and 3(c) to reveal that all the CNTs-coated silicons exhibit very good electron field emission properties. The electron field emission current density increases with Fe concentration in the  $\text{Fe}(\text{NO}_3)_3\text{-Si}(\text{OC}_2\text{H}_5)_4$ , Fe-Si-OR mixture. The electron field emission current density is around  $(J_e)_{0.01\text{M}} = 75 \mu\text{A}/\text{cm}^2$  at 5.5 V/ $\mu\text{m}$  applied field for the CNT layer



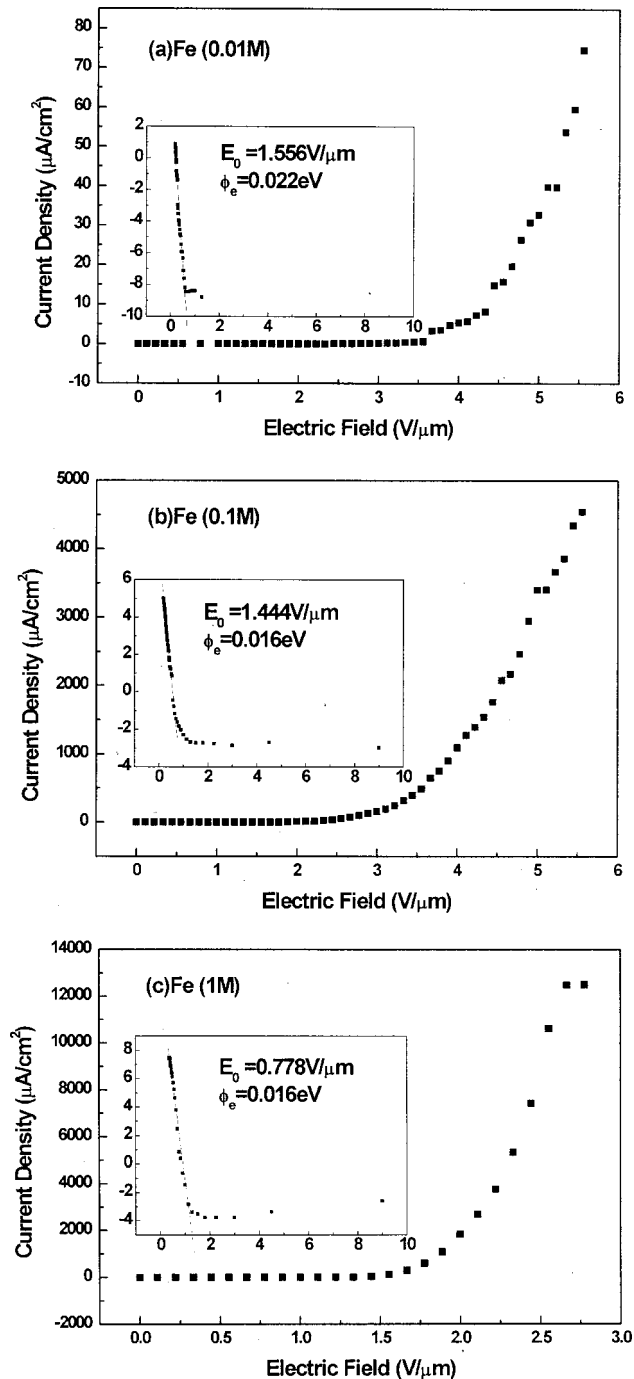


Fig. 3. Variation of electron field emission properties of CNTs grown on a  $\text{Fe}(\text{NO}_3)_3$ - $\text{Si}(\text{OC}_2\text{H}_5)_4$  catalyst mixture with the  $\text{Fe}(\text{NO}_3)_3$  concentration in the catalyst mixture.

grown on the 0.01 M Fe-Si-OR coated substrate. The  $J_e$  value of the CNT layer increases dramatically to  $(J_e)_{0.1 \text{ M}} = 4500 \mu\text{A}/\text{cm}^2$  and even to a value as high as  $(J_e)_{1 \text{ M}} = 13\,000 \mu\text{A}/\text{cm}^2$ , as the  $\text{Fe}^{3+}$  content in the catalyst mixture increases from 0.1 to 1 M, as shown in Figs. 3(b) and 3(c), respectively. Moreover, the turn-on field ( $E_0$ ) estimated from the FN plots decreases monotonously with concentration of  $\text{Fe}^{3+}$  in the catalyst mixture, viz,  $(E_0)_{0.01 \text{ M}} = 1.56 \text{ V}/\mu\text{m}$ ,  $(E_0)_{0.1 \text{ M}} = 1.44 \text{ V}/\mu\text{m}$ , and  $(E_0)_{1 \text{ M}} = 0.78 \text{ V}/\mu\text{m}$ .

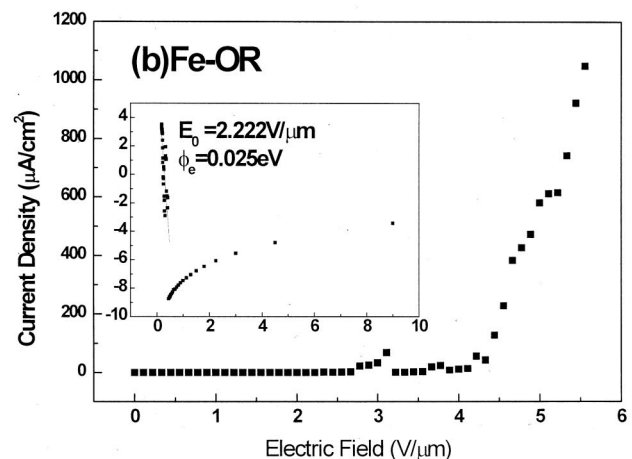
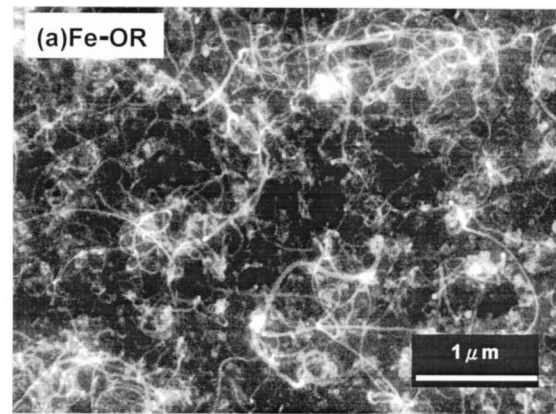


Fig. 4. (a) Morphology and (b) electron field emission properties of CNTs grown on Si substrates using  $\text{Fe}(\text{OR})_3$  as catalyst (OR= $\text{C}_7\text{H}_{17}\text{COO}$ ).

It should be noted that, although the electron field emission current density ( $J_e$ ) varies markedly as the Fe content of the catalyst mixture changes, the  $\varphi_e = \varphi/\beta$  ratio of the three CNT layers changes insignificantly, i.e.,  $\varphi_e = 0.016\text{--}0.022 \text{ eV}$  [cf. Figs. 3(a), 3(b), and 3(c)]. If we assume that the true work function ( $\varphi$ ) of the CNTs, which is a sheet of rolled  $sp^2$  network, is the same as the graphites [i.e.,  $(\varphi)_{\text{CNTs}} = 5 \text{ eV}$ ], we can estimate approximately that  $\beta = 1000$  for the CNTs shown in Fig. 2. These results infer that all of the CNTs, which emit electrons under the application of electric field, are of similar characteristics. The  $\text{Fe}^{3+}$  content in the catalyst mixture does not alter the diameter, the length, or the electron field emission behavior of individual CNTs. The larger electron field emission current density for the CNT layer grown on 1 M Fe-Si-OR catalyst mixture [Fig. 2(c)] is mainly due to higher number density of the CNTs. Restated, the electron field emission properties of the CNTs insignificantly change with the conditions for synthesizing the CNTs. The detailed structure of the CNTs, viz, chirality, single wall/multiwall, open end/closed end, seems not to markedly influence the electron field emission characteristics of the CNTs. Therefore, the substrate pretreatment process is believed to be the most important factor modifying the elec-

tron field emission characteristics of the CNT layers grown by this technique.

To support the above-described arguments, the characteristics of CNTs synthesized on a different form of Fe catalyst were investigated. Figure 4(a) reveals that when spin coated Fe-alkoxides [(Fe(C<sub>7</sub>H<sub>17</sub>COO)<sub>3</sub>), Fe(OR)<sub>3</sub>], were used as a catalyst, CNTs can also be easily grown on the Si substrate using similar synthesizing parameters. The thus obtained CNTs also possess very good electron field emission properties [Fig. 4(b)]. It takes only  $E_0=2.2$  V/ $\mu$ m to induce the emission process and attain a current density about  $J_e = 1050$   $\mu$ A/cm<sup>2</sup> under 5.5 V/ $\mu$ m applied field. The effective work function of these CNTs ( $\phi_e=0.025$  eV) is about the same value as those grown on the Fe(NO<sub>3</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> catalyst mixture. By contrast, the CNTs can hardly form on dc-sputtered Fe films, no matter what are the synthesizing conditions.

#### IV. CONCLUSION

CNTs exhibiting good electron field emission properties have been successfully synthesized using a novel CVD process, in which the substrates were heated up by a susceptor via the absorption of microwaves. Morphology of the CNTs coated on the silicon substrate varies with the form of Fe catalyst coated. CNTs own largest number density and ex-

hibit largest emission current density when using spin coated 1 M Fe(NO<sub>3</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> as a catalyst. The electron field emission can be turned on at  $E_0=0.78$  V/ $\mu$ m, attaining  $J_e = 13\ 000$   $\mu$ A/cm<sup>2</sup> under 5.5 V/ $\mu$ m applied field, even though the CNTs are randomly oriented. These CNTs possess large enough electron field emission properties and have good potential for applications as electron emitters in field emission display.

#### ACKNOWLEDGMENT

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