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## Effect of interface barrier between carbon nanotube film and substrate on field emission

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The influence of interface barrier on field emission of carbon nanotubes (CNTs) was investigated theoretically and experimentally. A double-potential barrier model was proposed to calculate the electron tunneling probability through the interface and surface barriers. The calculation result reveals that the difference of the electron tunneling probability through the two barriers is responsible for the nonlinearity of the Fowler–Nordheim (FN) plots for the field emission of the CNTs. To verify this model, a series of the CNTs were synthesized on the Si substrates covered with different thicknesses of SiO<sub>2</sub> layers as the interface barrier. Based on their field emission properties, it was found that the FN plots of the field emission of these CNTs deviated from the FN law when the applied electric fields were over a critical value, which was strongly dependent on the thicknesses of the SiO<sub>2</sub> layer. Therefore, the interface barrier has an important role in determining the field emission property of the CNTs. The experimental results are consistent with the calculation result based on the double potential model. © 2009 American Institute of Physics.

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### I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted much attention as a field emitter material due to their high aspect ratio, high mechanical strength, good field emission stability, and excellent field emission characteristics.<sup>1,2</sup> During the last decade, much work has been performed to aim at achieving field emission devices based on CNTs, for example, the field emission display.<sup>3</sup> The field emission properties of the CNTs have also been widely investigated<sup>4,5</sup> and the characteristics of the CNT field emission were always interpreted within the framework of the classical Fowler–Nordheim (FN) law.<sup>6</sup> But the interpretation is not frequently satisfactory, which means that the experimental *I-V* curves of the CNT electron field emission deviate from the FN law at the range of high applied electric field (i.e., the nonlinearity of the FN plots).<sup>7–13</sup> Different explanations for the above-mentioned deviation have been proposed as follows: (1) space charge effects in the vacuum spacing may cause the deviation in the FN plots of the CNTs;<sup>7</sup> (2) the presence of adsorbates (adsorbed molecules or impurities) at the CNT apex can enhance the field emission at low applied electric field, which would be then removed at high applied electric fields, causing the current to saturate;<sup>8,9</sup> (3) the presence of a resistance in series with the emitter, for example, a weak CNT/substrate electrical contact can induce the current saturation at high applied electric fields<sup>10,11</sup> or a large voltage drop along the CNT emitter and at the CNT/substrate interface;<sup>12</sup> (4) after a highly imposed emission, structural deformation of the emitter from crystalline nanotube bundle to amorphous-type carbon fibers dete-

riorates the efficiency of the field emission either by increasing the resistance of the emitter or by decreasing the field enhancement factor of the emitter tips.<sup>13</sup> However, CNTs must be deposited on a substrate for their application in vacuum electronics, the interactions between the substrate and the CNTs will play an important role in the field emission. Especially the CNT/substrate interface barrier may be a key factor in limiting the field emission of CNTs because the electrons emitted from CNTs depend on the efficiency of the electron injection from substrate into one-dimensional nanostructural emitters.

In this paper, the effect of the interface barrier on the nonlinearity of the FN plots was investigated in detail. A double-barrier model has been used to explain the interface barrier effect. It was found that the field emission property of the CNTs was influenced by both the interface barrier and the surface barrier. The difference of the two tunneling probabilities under electrical field will lead to the nonlinearity of the FN plots. Furthermore, in order to experimentally investigate the effect of the interface barrier on the field emission property of the CNTs, we synthesized the CNTs on the Si substrates, which were intentionally covered with different thicknesses of the SiO<sub>2</sub> layer to act as the interface barrier. The experimental results agreed well with the numerical calculation based on the double potential barrier model.

### II. MODEL AND CALCULATION

Considering the process of electron transportation from the substrate to the CNTs, the field emission electrons would tunnel through two barriers. First, the electrons tunnel through the interface barrier between the CNTs and substrate and then transport in the CNTs. Second, they tunnel through

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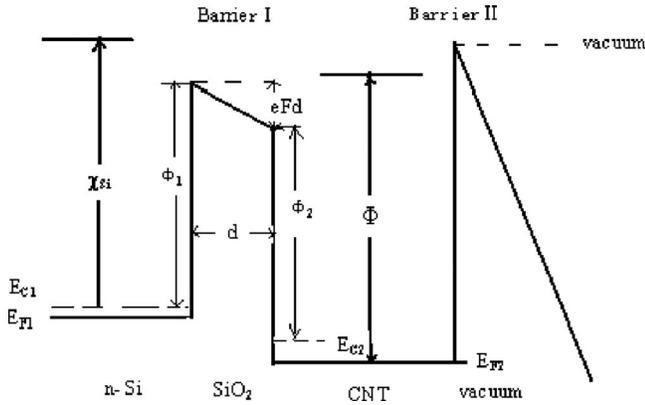


FIG. 1. Schematic illustration of the interface barrier and the surface barrier after applied electric field. Note that the potential barrier is not actually trapezoidal and triangular without considering an image potential and other factors.

the CNT/vacuum surface barrier and emit into the vacuum. Therefore, the double-barrier model<sup>14–17</sup> was used to explain the field emission process of the CNTs (Fig. 1). It was designed in our experiment that the SiO<sub>2</sub> layers with different thicknesses are specified as the interface barrier. In a previous work,<sup>18</sup> it was found that Si–C covalent bonds were formed between the CNTs and the substrate when the CNTs were deposited on the Si substrate or the SiO<sub>2</sub>/Si substrate by chemical vapor deposition (CVD) method. So our design may help us reveal the role of the interface barrier on the field emission characteristics of the CNTs.

Thus, we calculated the electron tunneling probability through the two barriers. The tunneling probability through the interface barrier of an electron with the energy of  $E_x$  can be expressed using the Wentzel–Kramer–Brillouin approximation,<sup>19</sup>

$$P(E_x) = \exp\left(-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m^*[U(x) - E_x]} dx\right), \quad (1)$$

where  $x_1$  and  $x_2$  are classical turning points,  $E_x$  is an electron energy moving along positive  $x$ -axis,  $m^*$  is the effective mass of electrons in the dielectric SiO<sub>2</sub> layer, and  $h$  is the Planck constant. A one-dimensional interface barrier potential model without the image force is given by

$$U_1(x, F) = \phi_1 + x/\varepsilon d(\phi_2 - eFd - \phi_1) + E_f (0 \leq x \leq d), \quad (2)$$

where the  $\phi_1$  is the barrier height between the SiO<sub>2</sub> and Si substrates in electron volts,  $\phi_2$  is the barrier height between SiO<sub>2</sub> and the CNTs in electron volts,  $d$  is the effective width of the SiO<sub>2</sub> barrier,  $\varepsilon$  is the relative dielectric constant of the SiO<sub>2</sub>,  $F$  is the external electric field (V/ $\mu$ m), and  $E_f$  is the Fermi energy of the Si. Considering the tunneling electron near the Fermi level<sup>20</sup> at room temperature, we have  $E_x = E_f$ . Substituting Eq. (2) into Eq. (1), the electron tunneling probability through the interface barrier is expressed as follows:

$$P_1 = \exp\{-8\pi d(2m^*)^{1/2}[\phi_1^{3/2} - (\phi_2 - eFd/\varepsilon)^{3/2}]/3h(\phi_1 - \phi_2 + eFd/\varepsilon)\}. \quad (3)$$

TABLE I. The constant and data in calculating of tunneling probabilities  $P_1$  and  $P_2$ .

$m_e$	$0.91 \times 10^{-31}$ (kg)
$m^* = 0.36m_e$	$0.33 \times 10^{-31}$ (kg)
$e$	$1.6 \times 10^{-19}$ (C)
$h$	$6.34 \times 10^{-34}$ (J S)
$\varepsilon$	3.9
$\beta$	500
$\chi_{Si}$	4.1 (eV)
$\chi_{SiO_2}$	0.95 (eV)
$\chi_{CNT}$	4.6 (eV)
$\phi_1$	$\chi_{Si} - \chi_{SiO_2} = 3.15$ (eV)
$\phi_2$	$\chi_{CNT} - \chi_{SiO_2} = 3.65$ (eV)
$d$	0.15, 0.20, 0.25 ( $\mu$ m)
$\Phi$	4.9 (eV)

On the other hand, the electron tunneling probability through the surface barrier can be represented as<sup>21</sup>

$$P_2 = \exp(-8\pi\sqrt{2m}\Phi^{3/2}/3he\beta F), \quad (4)$$

where  $\Phi$  is the work function,  $\beta$  is the field enhancement factor of CNT, and  $\chi$  is the electron affinity in Table I. The electron affinities<sup>22</sup> are 4.1 and 0.95 eV for Si and SiO<sub>2</sub>, respectively. The electron affinity of the CNTs is equal to that of graphite ( $\sim 4.6$  eV).<sup>23</sup> We choose the field enhancement factor of 500 for CNT according to Ref. 12 ( $\beta = 100$ –1000) and the real barrier widths  $d$  are 0.015, 0.020, and 0.025  $\mu$ m for SiO<sub>2</sub> layer, respectively. Substituting the above values in Table I into  $P_1$  and  $P_2$ , both the electron tunneling probabilities through the interface barrier and the surface barrier versus the electric field are showed in Fig. 2. The cross points of these curves are the critical electric fields  $E_{C1}$ ,  $E_{C2}$ , and  $E_{C3}$ , respectively.

Below the critical electric field  $E_C(E_{C1}, E_{C2}, E_{C3})$  ( $E < E_C$ ), the electron tunneling probability through the interface barrier ( $P_1$ ) is larger than that through the surface barrier ( $P_2$ ) ( $P_1 > P_2$ ). The tunneling electron through the interface barrier can supply enough electrons to tunnel through

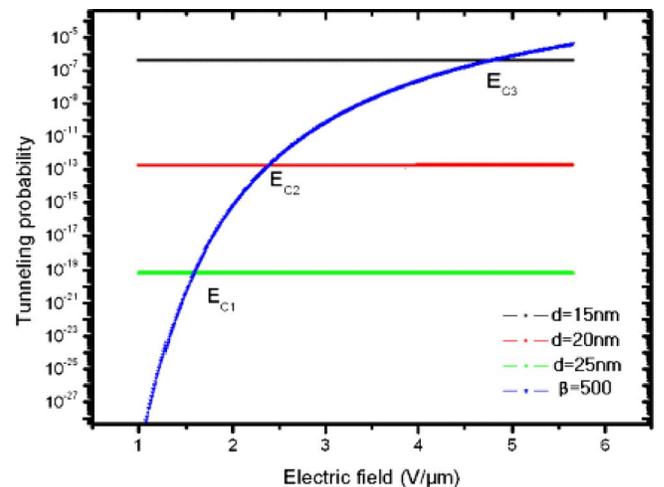


FIG. 2. (Color online) The electron tunneling probability of  $P_1$  through the interface barrier and that of  $P_2$  through the surface barrier vs applied electric field. (The CNT enhancement factor of  $\beta=500$  and the interface barrier widths  $d$  of 15, 20, and 25 nm, respectively.)

the surface barrier. The field emission current is dominated by the number of electrons tunneling through the surface barrier and the field emission process follows the FN law. Above the critical field  $E_C(E_{C1}, E_{C2}, E_{C3})$  ( $E > E_C$ ), the electron tunneling probability through the interface barrier ( $P_1$ ) is less than that through the surface barrier ( $P_2$ ) ( $P_1 < P_2$ ). The tunneling electron through the interface barrier cannot supply enough electrons to tunnel through the surface barrier. The whole electron field emission is hindered by the slow process of the electron injecting into the CNTs and the electron field emission does not follow the FN law. The plot of  $\ln(I/E^2)$  versus  $1/E$  will depart from the original line when above the  $E_C$ . So the nonlinearity characteristic of the FN plot will appear in the high electric field. The critical field  $E_C$  is determined by the barrier width of the interface.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

Doping levels in the substrates can change Fermi level and the CNT field emission can be influenced by the substrate. In our previous experiments, we deposited CNTs on different doping level substrates covered with the same thickness of  $\text{SiO}_2$  layer. The FN plots had no obvious difference in our test voltage region because the variation in the barrier height was very smaller than that of  $\text{SiO}_2$  dielectric barriers. In this work, in order to eliminate the effect of doping levels on the CNT field emission, we chose the same Si substrate. So we could not further consider the influence of substrate effect.

The CNTs were grown by CVD. The substrates are the heavily doped *n*-type (100) silicon with high conductivity ( $\rho = 0.014 \Omega \text{ cm}$ ) and the sample (100) Si covered with different thicknesses of the  $\text{SiO}_2$  layer. The Si substrate was treated in 1% HF solution for 5 min to remove the native  $\text{SiO}_2$ . The  $\text{SiO}_2$  layers with the different thicknesses were formed by wet oxidization of the Si wafer at 1100 °C for 2, 3, and 5 min, respectively. The thicknesses of the  $\text{SiO}_2$  layers were measured by scanning electron microscopy (SEM), which are 15, 20, and 25 nm, respectively. The Fe catalyst particles were deposited on the substrates by ion beam sputtering at room temperature. After deposition, the substrates were first annealed at 850 °C in a hydrogen atmosphere for 1.5 h in a quartz-tube furnace. Then, the CNTs were grown at 1000 °C in a gas mixture of methane [400 SCCM (SCCM denotes cubic centimeter per minute at STP)] and hydrogen (30 SCCM) for 15 min. The surface morphology of the CNT bundles was observed by SEM, as shown in Fig. 3. The CNTs on all substrates are randomly oriented and entangled with each other. The inset of Fig. 3 showed an image of an individual CNT partly embedded in the substrate surface to form the Si-C covalent bonding similar to previous report.<sup>18</sup>

The screening effect plays a crucial role on CNT field emission properties. But integrated field emission measurements on CNTs with various densities of CNTs did not reveal significant differences in their emission properties.<sup>24</sup> Many repeated experiments had been carried out and a larger number of samples had been obtained. We chose the samples of CNTs with the similar morphology and density. So the screening effect on CNT field emission could be neglected in

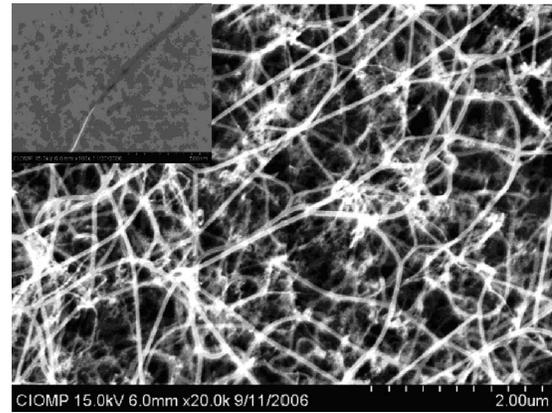


FIG. 3. Surface morphology of typical CNT films on  $\text{SiO}_2$  layer-covered Si substrate. The inset gives the detail of a CNT partly embedded in substrate to form a Si-C covalent bonding.

the range of the error in our contrasted experiments. The differences of emission behavior should be primarily attributed to interface effect.

In order to study the field emission characteristic of the CNTs, they were put into a vacuum chamber with the base pressure lower than  $9 \times 10^{-5}$  Pa. The samples were used as a cathode and the indium tin oxide glass was used as an anode. The distance between the cathode and anode was 300  $\mu\text{m}$ . To carry out the field emission measurements, the current-applied electric field curves were collected by a Keithley 237 source measure unit. Figure 4 presents the FN plots of  $\ln(I/E^2)$  versus  $1/E$ . The FN plots show a nonlinear characteristic and exhibit a critical field (or knee  $E_C$ ). The FN plots deviate from the original line when the applied electric field is above the  $E_C$  because the electron tunneling probability of the interface barrier ( $P_1$ ) is less than that of the surface barrier ( $P_2$ ). Below the critical electric field  $E_C$ , the electron tunneling probability of the interface barrier ( $P_1$ ) is larger than that of the surface ( $P_2$ ) and the field emission will fol-

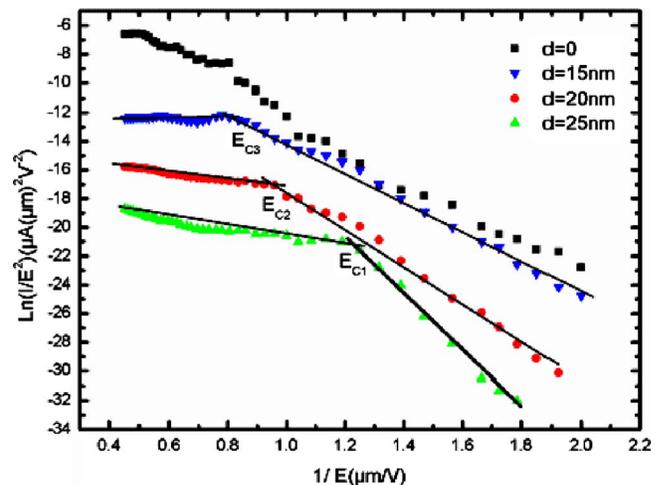


FIG. 4. (Color online) The FN plots of  $\ln(I/E^2)$  vs  $1/E$  for CNT field emission on Si substrates covered with different thicknesses of  $\text{SiO}_2$  layers and Si substrate without thermal oxidation.  $E_{C1}$ ,  $E_{C2}$ , and  $E_{C3}$  are critical electric fields of the FN plots for CNT field emission on Si substrates covered with different thicknesses of  $\text{SiO}_2$  layers ( $d = 15, 20,$  and  $25$  nm), respectively.

low the FN law. The FN plot of the CNTs grown on the Si substrates without thermal oxidation has no distinct  $E_C$  in our experimental voltage region because the interface barrier between the CNT and the substrate is lower and thinner. Our experimental results further verified the above numerical calculation.

The electron transport and field emission through interface barriers and surfaces have been studied by many researchers in recent years.<sup>25–28</sup> It was found that the FN plot had two slopes when GaN nanorod films<sup>29</sup> were deposited on Si substrates with native silicon oxide layer because of the existence of parasitic resistance in the GaN/SiO<sub>2</sub>/Si sample. CNTs were grown on different substrates (SiO<sub>2</sub>, Al, Cu, and Ti) and it was found that there were explicit knees in FN plots.<sup>17</sup> Our findings agree with the experimental results of Cui *et al.*<sup>11,30</sup> that carbon film field emission follows FN law in the low-field region and deviates from the FN law in the high-field region because of the two variable resistances of surface and interface or emitter itself.

#### IV. CONCLUSIONS

The effect of the interface barrier on CNT field emission is quantitatively analyzed by the double-barrier model using the classical quantum mechanism theory. The electron tunneling probability through the interface and surface barriers, respectively, is calculated. The calculation result reveals that the difference of the electron tunneling probability through the two barriers is responsible for the nonlinearity of FN plots for the field emission of the CNTs. The field emission of the CNT films on the Si substrates was covered with different thicknesses of the SiO<sub>2</sub> layers as the interface barrier was investigated. The experimental results agree well with the calculated ones. This paper illuminates the effect of the interface barriers on the field emission and these findings could provide us a deeper insight way to understand further the field emission of CNTs.

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