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## Oxygen and ozone oxidation-enhanced field emission of carbon nanotubes

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Vertically aligned carbon nanotube (CNT) arrays were grown on *p*-type silicon wafer using acetylene and iron phthalocyanine as the sources of hydrocarbons and catalysts, respectively. The CNT arrays were treated by chemical reagents, such as oxygen ( $O_2$ ), ozone ( $O_3$ ), bromine, and acids. When treated by  $O_2$  and  $O_3$ , the emission current of the CNT array was increased ~800% along with a decrease of the onset field emission voltage from 0.8 to 0.6 V/ $\mu$ m. Other chemical treatments, e.g., bromination and acid oxidation, lead to poorer field emission performance. The effects of these chemical processes on the field emission properties of CNT arrays will be discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1485315]

Since the first report of using carbon nanotubes (CNTs) as field emitters,<sup>1</sup> the study of CNT field emission has become one of the major areas of research for CNT nanomaterials.<sup>2–11</sup> Field emission properties of CNT films prepared from both screen printing of CNT slurry (i.e., the postgrowth method)<sup>2-4</sup> and *in situ* growth of CNT arrays from chemical vapor deposition (CVD) methods have been reported.<sup>5-13</sup> Although the screen-printing method has the advantages of low cost and ease of preparation, it suffers from the drawback of few vertically aligned CNTs and thus low current density as well as a high onset emission voltages.<sup>2-4</sup> To have good field emission behavior (i.e., low onset of field emission voltages and large emission currents), the emitters should have small, sharp tips with orientation perpendicular to the cathode surface. In the literature, preparation of vertically aligned CNT arrays via CVD was achieved by growing CNTs out of the nanochannels of a mesoporous silica substrate<sup>5</sup> using NH<sub>3</sub> plasma treated nickel thin film as the catalyst,<sup>6</sup> or using iron phthalocyanine as the source of both the hydrocarbon and metal catalysts.<sup>7</sup> In the first method, all CNTs were forced to grow along the direction of the nanochannels. For the latter two processes, the mechanisms for the growth of well-oriented CNT arrays are not clear, and are generally attributed to the overcrowding effect, i.e., the sterical hindrance and van der Waals attractions among growing CNTs. The onset emission voltages of vertically aligned CNT arrays from the CVD process were reported to be in the range of  $4-0.9 \text{ V}/\mu\text{m}$ .<sup>8-11</sup> Recently, Lee and co-workers<sup>12</sup> grew CNT arrays on iron/silica substrates. The CNT film was then peeled off and reversed to allow the bottom side (with open CNT tips) to face upward. With open ended CNTs, a very low turn-on voltage of 0.6–1.0 V/ $\mu$ m was observed.

In this study, we grew CNT arrays by the CVD method and subsequently treated the vertically aligned CNT arrays with various chemical reagents, such as  $O_2$  and  $O_3$ , bromine and acids. Growth of a vertically aligned CNT array on a *p*-type silicon wafer was conducted similarly to a procedure in the literature.<sup>7</sup> Briefly, 0.1 gram iron phthalocyanine (FePc) and a *p*-type Si wafer were put into a tube furnace at 850 °C under gas flow (5% acetylene in Ar, flow rate: 10 sccm) at 1 atm for 30–60 min. Thermal pyrolysis of FePc provides nanosized Fe particles for catalytic decomposition of acetylene, which leads to growth of the vertically aligned CNT array. Scanning electron microscope (SEM) images of the CNT array show that the CNTs are quite perpendicular to the substrate surface (see supplementary Fig. S1<sup>22</sup>). Transmission electron microscope (TEM) measurements show that the CNTs are multiwalled and have 40–50 layers. Raman measurement shows two bands at 1345 and 1576 cm<sup>-1</sup> (see supplementary Fig. S2<sup>22</sup>), which are characteristic bands of CNTs grown by the CVD method.<sup>13</sup>

The field emission property of the CNT array was measured using ITO glass as the anode and a glass plate of 200  $\mu$ m thickness as the spacer to separate the CNT cathode from the ITO anode. The voltage applied was controlled by a Keithley electrometer (model 237), and the field emission current was measured by the same electrometer. The whole setup was in a vacuum chamber of 10<sup>-6</sup> Torr. As shown in Fig. 1 (open circle), at an applied voltage of 4.5 V/ $\mu$ m, the current density reaches a value of ~10  $\mu$ A/cm<sup>2</sup>. According



FIG. 1. Current–voltage plots of CNT arrays under different conditions: an as-grown CNT array (open circle) and the authentic CNT array treated by  $O_2$  oxidation at 400 °C for 10 (closed triangle), 20 (open triangle), and 25 min (star). The inset is the  $\ln(J/E^2)$  vs 1/E plots of the four CNT arrays shown, where J is the current density and E is the voltage applied.

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to Fowler-Nordheim field emission theory, the plot of  $\ln(J/E^2)$  vs 1/E (where J is the emission current density and *E* is the voltage applied) will have a linear relationship. The Fowler–Nordheim (FN)  $[\ln(J/E^2)$  vs 1/E] plot of the device (see the inset in Fig. 1, closed triangle) shows a quite linear pattern with the onset of electron emission voltage (the turning point, shown by the arrow) of 0.8 V/ $\mu$ m, indicating that the field emission is intrinsically driven by the electric field.

To modify the electronic properties, CNT arrays grown on a p-Si wafer under the same conditions were treated with various oxidants, such as O<sub>2</sub>, O<sub>3</sub>, Br<sub>2</sub>, and acids. In the case of O<sub>2</sub> oxidation, the CNT array on the *p*-Si substrate was put in an oven at 400 °C for 10, 20, and 25 min in the presence of air  $(O_2)$ . As shown in Fig. 1, the field emission of the CNT array with 10 min O<sub>2</sub> treatment (closed triangle) is about the same as that of the original sample. However, the samples with 20 (open triangle) and 25 min (star) O<sub>2</sub> oxidation have much larger emission currents at the same applied voltages. At an applied voltage of 4.5 V/ $\mu$ m, the emission current was enhanced from 9 to 72  $\mu$ A/cm<sup>2</sup> (or an eightfold increase) after 20 min O<sub>2</sub> treatment at 400 °C. Meanwhile, the onset field emission voltage (see the turning point in the FN plot) changes from 0.8 to 0.6 V/ $\mu$ m. TEM shows that the end tips of many CNTs were opened or partially opened after the  $O_2$  oxidation process (see Fig. 2). Evidently, the increase in the field emission current and the decrease in the onset field emission voltage observed in Fig. 1 are due to opening of the CNT end tip by the O2 oxidation process. As reported before by Smalley *et al.*,<sup>1</sup> by Lee and co-workers<sup>12</sup> and by Wang et al.,<sup>14</sup> open-ended CNTs have sharper tips, and thus lower onset field emission voltage as well as higher emission current. The emission current is not only determined by the sharpness of the emitter tips, it is also affected by the conductivity of the emitters. In the array format, all highly strained CNT tips are exposed to air and are readily oxidized by O<sub>2</sub> first before oxidation of the less strained CNT walls, which are partially protected from being oxidized by the array configuration. However, prolonged O<sub>2</sub> oxidation will lead to damage along the CNT walls, and thus a gradual decrease in emission current. Selective and preferential oxidation at the CNT tips is the feature of the current process. Previously, it was reported<sup>15</sup> that open-ended multiwalled nanotubes (MWNTs) have much poorer field emission properties than close-ended MWNTs, when the open-ended MWNTs were prepared by O<sub>2</sub> oxidation of carbon soot at high temperatures. Under the carbon soot-O<sub>2</sub> oxidation condition, most of the CNT tips were buried within the powder, and a lot of CNT walls were exposed to O<sub>2</sub> oxidation. Only a small percent of open-ended MWNTs was left after the oxidation process. Serious oxidative damage along the tube walls of the surviving MWNTs is most likely responsible for the reported poor field emission performance.<sup>15</sup> The FN plots of  $O_2$  treated samples (see the inset in Fig. 1) show a linear slope at the low applied voltage region and a smaller slope at the high voltage region. This type of FN pattern for MWNT field emitters was observed before, and the smaller FN slope at high voltage region is attributed to the saturation effect of the emitters.<sup>15</sup>

Besides O<sub>2</sub> oxidation, ozone is also known to react with olefins and lead to cleavage of C=C double bonds.<sup>16</sup> As



FIG. 2. TEM images of CNTs from a CNT array which was treated by O2 oxidation for 20 min at 400 °C.

shown in Fig. 3, the sample with 3 min  $O_3$  treatment at room temperature has an ~7.5-fold increase in emission current together with a decrease in onset emission voltage from 0.8 to 0.6 V/ $\mu$ m. Prolonged (5, 7, or 9 min) O<sub>3</sub> treatment leads



FIG. 3. Current-voltage plots of CNT arrays treated under different conditions: an as-grown CNT array (open circle) and CNT arrays treated by O3 oxidation at room temperature for 1 (open inverted triangle), 3 (open 128.83.63.20 square), 5 (open triangle), 7 (star), 9 (+) min, and by  $Br_2$  gas (×).

to a decrease in emission current from the maximum (at 3 min), which, however, is still significantly better than that of the authentic sample. It was reported that CNT end tips became sharp when treated with ozone.<sup>17</sup> Due to the array configuration,  $O_3$  preferentially attacks the exposed CNT tips, similar to in the  $O_2$  case. Prolonged (5, 7, and 9 min) treatment of  $O_3$  most probably leads to oxidative damage along the CNT walls and thus a decrease in emission current. It should be noticed that the reaction condition of  $O_3$  is much milder than the  $O_2$  condition (room temperature versus 400 °C; vs 20 min), which is due to the higher chemical reactivity of  $O_3$  to olefins than  $O_2$ .<sup>18</sup>

In addition to the  $O_2$  and  $O_3$  treatments, the effect of  $Br_2$ treatment was also studied (see  $\times$  in Fig. 3). Treatment of Br<sub>2</sub> gas at room temperature for 20 min leads to only slight changes in both the emission current and turn-on voltage (see  $\times$  in Fig. 3). Smalley and co-workers<sup>19</sup> reported that exposing single-walled nanotube (SWNT) bucky paper to Br<sub>2</sub> leads to an increase in the conductivity of the SWNT paper. It was rationalized that Br2 serves as an electron acceptor that oxidizes CNTs and creates "holes" in SWNT ropes which then leads to an increase in the conductivity. However, besides the electron transfer oxidation process (a nonchemical bond formation process), Br<sub>2</sub> can also undergo chemical reactions with the olefin bonds of CNTs at both the tube wall and tip region and form C-Br bonds.<sup>20</sup> The former process creates free moving holes on the CNT wall and is favorable to CNT conductivity; the latter process destroys the conjugate system and thus decreases the CNT conductivity. In the current study, the observation of slight changes in the conductivity of the CNT array is probably from combined (cancellation) effects of the above two processes.

Besides bromination, as-grown CNT arrays were also treated by immersion in an acid mixture (concentrated  $H_2SO_4$  and  $HNO_3$  in a 3:2 volume ratio) at room temperature for 30 min, followed by gentle washing in de-ionized water and vacuum drying. The final CNT array was found to have negligible emission current (data not shown) and the CNT film very easily fell off. Most probably, the acid treatment leads to poorer physical contact between the CNTs and the supporting substrate via dissolution of metal nanoparticles at the roots of CNTs. Treatment of CNT arrays by other oxidants, such as NO or NO<sub>2</sub> gases, leads to poorer field emission performance (data not shown). Only oxidants, which are capable of cleaving C==C double bonds, are able to cut open CNT tips and improve field emission performance.

In summary, we have demonstrated a facile gas phase  $O_2/O_3$  oxidation process for improvement of the field emission properties of CNT arrays via selective opening of the CNT tips in the array format with minimum damage along the tube walls. With the  $O_2/O_3$  oxidation treatment, the onset emission voltage of CNT arrays can be lowered to ~0.6 V/ $\mu$ m along with 700%–800% enhancement in the emission current. The sharper the CNT end tip, the lower the onset emission voltage as well as the larger emission current. The current gas phase  $O_2/O_3$  oxidation method is a very simple, convenient, clean process that can be very easily applied to any CNT array/film to lower the CNT onset emission voltage and enhance the emission current.<sup>21</sup>

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- <sup>21</sup> A reviewer pointed out that the emission current of our CNT array is small compared to some values in the literature. The magnitude of CNT emission current is strongly dependent on the number of CNTs in a unit area as well as on the electric conductivity of CNTs, which is a characteristic of a given CNT growth process. The main emphasis and the unique feature of our work are the cap opening of CNT arrays (and thus the enhancement in the field emission current), rather than the preparation of vertically aligned CNT arrays.
- <sup>22</sup> See EPAPS Document No. E-APPLAB-80-058223 for two figures entitled "Oxygen and ozone oxidation-enhanced field emission of carbon nanotubes." This document may be retrieved via the EPAPS homepage (http:// www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

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