Field emission from aligned carbon nanofibers grown in situ by hot filament chemical vapor deposition

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Field emission from aligned carbon nanofibers grown *in situ* by hot filament chemical vapor deposition

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Aligned high-aspect-ratio carbon nanofibers were grown *in situ* using modified hot filament chemical vapor deposition. The field-emission properties were then studied. An Fe–Cr wire filament acted as a catalytic source and a heat source. Carbon nanofibers were deposited on a Si substrate with CO_2 as a carrier gas through ethanol. The experimental results indicate that the flow in the horizontal direction to the substrate produces carbon nanofibers with diameters of less than 10 nm. The field-emission current of 2 V/μm was 0.54 mA/cm^2; the turn-on field of the sample was 1.1 V/μm. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1568163]

Field-emission display is evolving as a promising technique for manufacturing the next generation of flat panel displays (FPD). Indeed, much effort has been made to make metal-tip emitters and silicon-tip array field-emission devices.[1] However, the electrical field required to trigger the field emission of such devices is quite high. Moreover, their performance rapidly deteriorates due to thermal effects, causing serious contamination and damage to the emitter materials. A good candidate for field emitters must have a high-aspect-ratio structure, low work function, and stable chemistry properties. For applications such as FPDs, large-area films of nanotubes,[2,3] or nanofibers,[4,5] which produce uniform field emissions across the surface are required. Dense aligned fibers normal to the substrate can further enhance the field emission and the uniformity of such emission.

Recently, Chen *et al.*[6] grew aligned graphitic nanofibers on single crystalline Ni(100) substrate by plasma-assisted hot filament chemical vapor deposition (HFCVD) using a gaseous mixture of nitrogen and methane. Small Ni particles generated by the plasma on the surface of the substrate catalyzed the growth of nanofibers with diameters of 100–200 nm and a density of 10^8/cm^2. The method was extended to synthesize thinner aligned graphitic nanofibers with greater packing density by modifying the deposition process.[4] However, the thinnest nanofibers they obtained were 30 nm. Our recent study reported a simple, nontoxic, inexpensive *in situ* HFCVD method for preparing multiwalled nanotubes on silicon.[7] The method uses a filament as the heat source for pyrolysis and catalytic evaporation of the Fe–Cr filament. In this study, using our method, nanotubes and nanofibers were deposited when the carrier gas flowed vertically and horizontally to the substrate, respectively. Thinner nanofibers were developed and applied in field emission.

Our earlier report described the simplified chemical vapor deposition (CVD) method for synthesizing carbon nanotubes.[7] The apparatus used for synthesis is similar to that used to deposit CVD diamond. However, tungsten is the filament material most commonly used in diamond deposition. Here, an Fe–Cr wire is coiled as a filament to grow nanotubes and nanofibers. Such an Fe–Cr wire is frequently used in furnace heating. The wire is not high grade and has several impurities, being composed of Fe (72.43%), Cr (23.42%), Mn (3.45%), and Ni (0.69%). Deposition needed not be *in vacuo*, and process pressure was closed to the atmosphere. Carbon nanotubes and nanofibers were deposited on the Si substrate with CO_2 as a carrier gas that passed through ethanol. Different directions of flow of CO_2 onto the substrate were adopted to confirm the effect of deposition conditions by adjusting the position of the gas inlet nozzle. The system used a 1 mm diameter Fe–Cr wire, and was heated by an ac current of 22 A at 40 V. In this experiment, the temperature of the filament was approximately 1200 °C, which was 100–200 °C lower than its melting point. The distance of the filament to the sample was 2 mm. The growth proceeded for 15 min.

After deposition, each sample was first visually examined. The surface of the sample near the bottom of the coiled filament was the blackest. The location of the nanofibers on the sample was examined using a scanning electron microscope (SEM). The images reveal that most nanofibers were near the bottom of the coiled filament. Figure 1(a) displays the SEM image of these nanofibers. These nanofibers were produced when CO_2 carrier gas flowed horizontally to the substrate. Bundles of nanofibers are observed on the center of the substrate. The nanofibers have a high-aspect ratio, implying good field-emission characteristics. Figure 1(b) shows SEM image of nanotubes obtained using CO_2 carrier gas which flowed vertically toward the substrate. A fixed CO_2 flow rate of 15 sccm yielded two completely different morphologies. Figure 1(b) shows a random tube network that consists of numerous curved tubes was formed; the tubes are 50–70 nm in diameter and a few tens of microns long. We supposed that flow direction should change the distribution and particle size of catalysts which originated from a filament on the silicon sample.

The carbon nanofiber in Fig. 2, referred to in Fig. 1(a), is clearly solid in contrast to the hollow structure of the carbon nanotube. The insertion in Fig. 2 displays a transmission electron microscope (TEM) image of an end section of an individual nanofiber. The structure is similar to that of a car-

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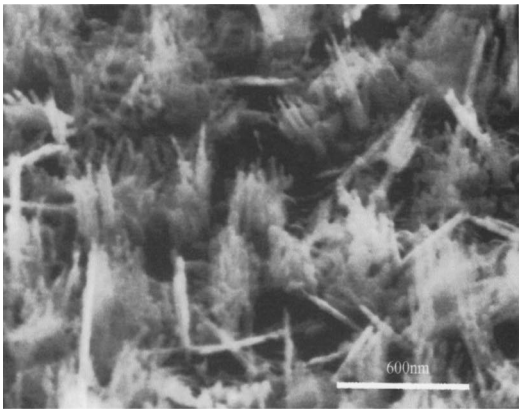
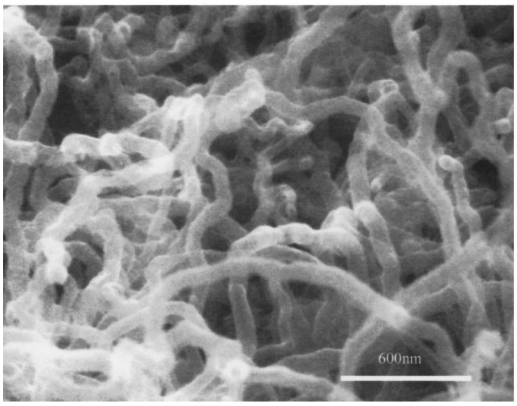


(a) Horizontal flow



(b) Vertical flow

FIG. 1. SEM images of two carbon nanostructures on silicon samples. (a) Nanofibers are obtained with CO_2 carrier gas that flows horizontally and (b) nanotubes are obtained with CO_2 carrier gas that flows vertically.

bon fiber, but with a nanosized diameter. Under both growth conditions, the temperature of samples was almost the same (~700 °C). Therefore, carbon nanofibers with a diameter of 10 nm can be grown using this HFCVD method by simply adjusting the direction of flow of the carrier gas. The diameters of the fibers are smaller than those obtained in other reports which mostly include diameters of 30–100 nm.[4]

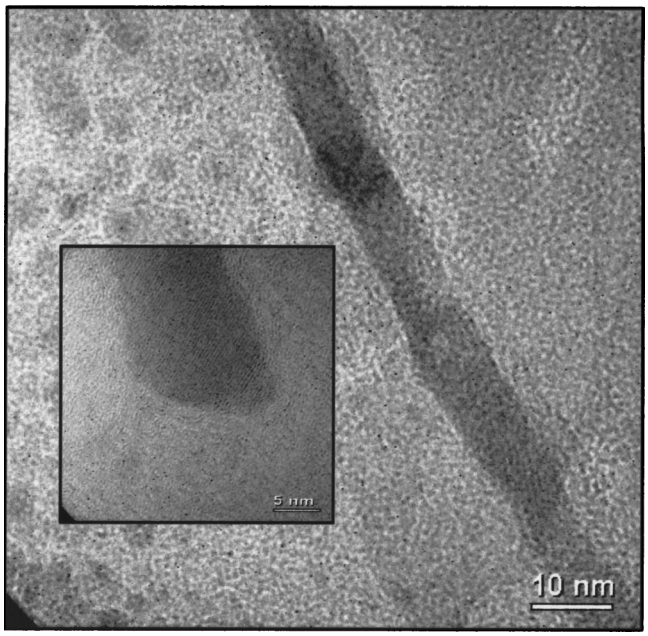


FIG. 2. TEM images of nanofiber, obtained with CO_2 carrier gas that flows horizontally.

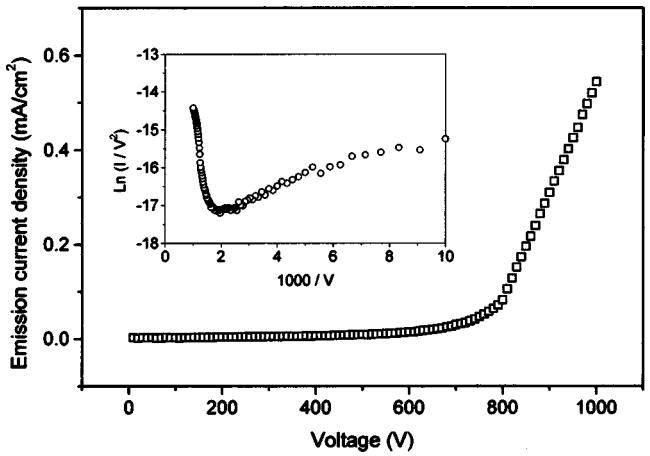


FIG. 3. Emission current density against applied voltage and the F–N plot for the nanofibers, obtained with CO_2 carrier gas that flows horizontally.

Figure 3 displays the electron-emitting characteristics of the nanofibers obtained using a diode structure. An anode, indium tin oxide glass, was separated by 500 μm from the tip of the cathode made of nanofibers. The current–voltage properties were measured using an electrometer (Keithley 237) and analyzed through the Fowler–Nordheim (F–N) model. The emission current at an applied voltage of 1000 V was 0.54 mA/cm^2. The macroscopic turn-on field, which is the field needed to extract a current density of 10 μA/cm^2, was 1.1 V/μm. One report[8] concluded that a comparison among film field emitters is pertinent only if the field-emission measurements, especially the interelectrode distance and geometry, were taken under the same experimental conditions. However, the field enhancement factor, β, is to be extracted using a commonly used method.

In 1928, Fowler and Nordheim proposed the model of field emission from a solid.[9] The F–N model states that the relationship between the emitted current in the local electric field F and the work function φ is $I \propto (F^2/\varphi)\exp(B\varphi^{3/2}/F)$, with $B = 6.83 \times 10^9$ (VeV$^{-3/2}$ m^{-1}). The local electric field F is not simply V/d, which is the macroscopic field obtained with an applied voltage V between two electrodes separated by a distance d. Rather, F is, in most cases, larger by an enhancement factor β, which reflects the ability of the emitter to amplify the field. β is determined mostly by the geometrical shape of the emitter, and the field at the emitter surface is frequently expressed as $F = \beta E = \beta V/d$, where $E = V/d$ is the macroscopic field. Moreover, literature includes arguments based on values of β that have been determined from the shape of the emitter, and especially from its radius of curvature at the tip, R_{tip}. The most basic approximation is $F \approx V/(k \cdot R_{\text{tip}})$, where k is a constant that depends on the geometry and is taken to be equal to 5 for an infinitely long cylindrical emitter.[10] From the aforementioned definition and approximation for F, $\beta = d/(k \cdot R_{\text{tip}})$ is obtained. Thus, $R_{\text{tip}} = 10$ nm yields $\beta = 10\,000$.

In summary, a modified HFCVD method is reported for synthesizing *in situ* carbon nanofibers, using CO_2 as a carrier gas through ethanol. Nanotubes and nanofibers were deposited when the carrier gas flowed vertically and horizontally

to the substrate, respectively. However, this study demonstrates that the uniformity of the nanofibers grown on the sample must be further improved, especially with respect to filament configuration since the sample surface near the bottom of the coiled filament was blackest, and revealed that most nanofibers were grown here. Aligned carbon nanofibers with diameters of less than 10 nm were formed, and related field-emission properties were measured. In the experiment, the carbon nanofibers showed field-emission characteristics that included a turn-on field of 1.1 V/μm and an emission current of 0.54 mA at 2 V/μm.

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