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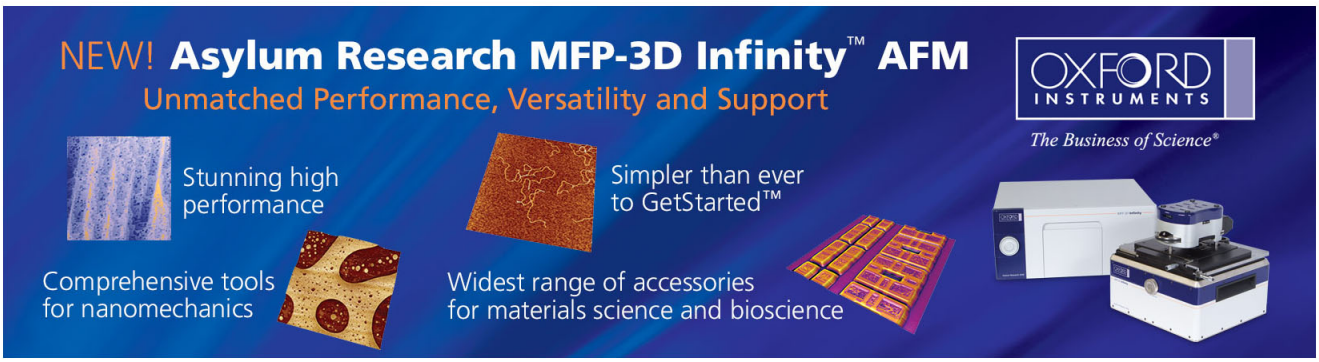

Self-embedded nanocrystalline chromium carbides on well-aligned carbon nanotips

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Well-aligned carbon nanotips embedded with nanocrystalline chromium carbide were directly grown on a substrate by microwave plasma chemical vapor deposition. These nanomaterials grew up to about 1 μm long and 60 nm in diameter, yielding a high aspect ratio. In comparison between carbon nanotubes with hollow structure, transmission electron microscopy images show its solid body, which is made of graphite along with nanocrystalline chromium carbide on the tip. These nanomaterials perform well in field emission applications with a turn-on field of 1.38 V/μm and 565 μA/cm^2 at 2.2 V/μm. Our result confirms the possibility of the self-embedded nanocrystalline materials on the top of carbon nanotips. © *2003 American Institute of Physics.*
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Carbon can bond in different ways to create structures with very different properties. Since the discovery of carbon nanotubes in 1991,[1] the synthesis of carbon-encapsulated composite nanostructure has attracted much attention. Experiments on nanotubes imply that they are suitable for use in many applications, such as scanning microscope probes[2] and electron field emitters.[3–5] The introduction of metals into multiwalled carbon nanotubes may significantly alter their conducting, electronic, and mechanical properties, as well as altering the properties of the metal.

This study describes nanocrystalline particles capped on the top of the carbon nanomaterials. The aim of this letter is to contribute to the characterization of well-aligned carbon nanotips with embedded of nanocrystalline chromium carbides (CNTWNCCs). These nanocrystalline particles offer a confined space in which nanoscience can be conducted. Restated, these metal nanoparticles act as templates rather than catalysts. The presented results show the possibility of the self-embedded nanoparticles on the top of the carbon nanotips.

Starting substrates were mirror-polished *n*-type, (100) oriented Si wafers with a resistivity of 4.5–5.5 Ω/cm. Wafers were cleaned by Radio Corporation of America cleaning process to remove contamination on the silicon surface. After cleaning, a SiO_2 dielectric layer was deposited using a high-temperature and low-pressure furnace deposition system (model ASM LB-45). A 150-nm-thick film of Cr was deposited on SiO_2 by using a dual electron-gun evaporator (model ULVAC EBX-10C, Japan). Then, substrates underwent microwave plasma chemical vapor deposition to grow CNTWNCCs. Before deposition, H_2 plasma treatment was used to activate the chromium films and then to clean the surface of the substrate. The reactive gases used in deposition were CH_4/H_2 with the flow rate of 10/25 sccm. The growth temperature, pressure, and time were 800 °C, 15 Torr, and 30 mins, respectively. During deposition, a −120 V bias was applied to the samples.

After deposition, the produced CNTWNCCs were characterized using a scanning electron microscope (SEM) to observe their length and morphology. High-resolution transmission electron microscope (TEM) and energy dispersed spectrum (EDX) were used to determine the nanostructure of individual CNTWNCCs and the component of nanocrystalline materials. An $I-V$ measuring system was used to obtain the field emission property.

Figures 1(a) and 1(b) show the cross-section and top view morphology of CNTWNCCs. It is found that each uniform CNTWNCC is significantly well-aligned to the substrate. In addition, Fig. 1(c) clearly displays the nanocrystalline chromium carbide on the top of the well-aligned carbon nanotips. Many studies about aligned carbon nanotubes also have been reported elsewhere.[6–8] However, high-magnification SEM pictures show that partial carbon nanotubes are not well aligned. Strictly speaking, this result implies that alignment is a macroscopic property, not an individual phenomenon: a bundle of carbon nanotubes is aligned. Initially, H_2 plasma pretreatment is used not only to clean the surface of the substrate, but also to activate the Cr film into nanoparticles on the substrate, offering a confined space for the growth of carbon nanotips. As growing carbon nanotips, the Cr nanoparticles are lifted off from the substrate and carburized into nanocrystalline chromium carbides. Our previous work have been explained the growth mechanism of carbon nanotips.[9] The final generation of Cr particles may be due to the interaction between Cr and the substrate. The growing carbon nanotips gradually lift-off the Cr particles because of the weak force between Cr and the substrate. This growth mechanism is analogous to the tip-growth model of carbon nanotubes.[10] It is worth emphasizing that the optimum H_2/CH_4 ratio for generating CNTWNCCs is 25/10 sccm. Once the ratio beyond 25/10 sccm, meaning the concentration of carbon is increased, higher growth rate of the nanotips causes the coalescence of individual nanotip to become continuous films. As the ratio exceeds 25/10 sccm, higher etching rate resulted from the decomposed hydrogen would reduce the size of Cr nanoparticles on the top

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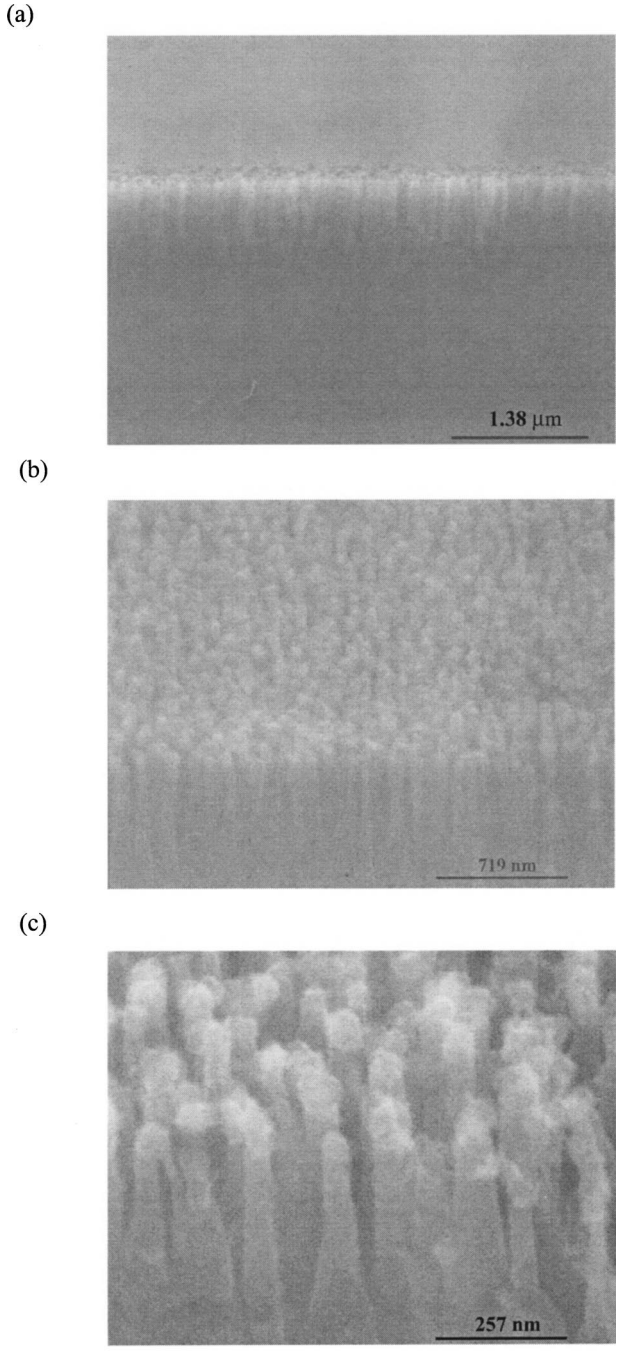

FIG. 1. SEM photographs of (a) cross-section view, (b) top view, and (c) high magnification images of CNTWNCCs.

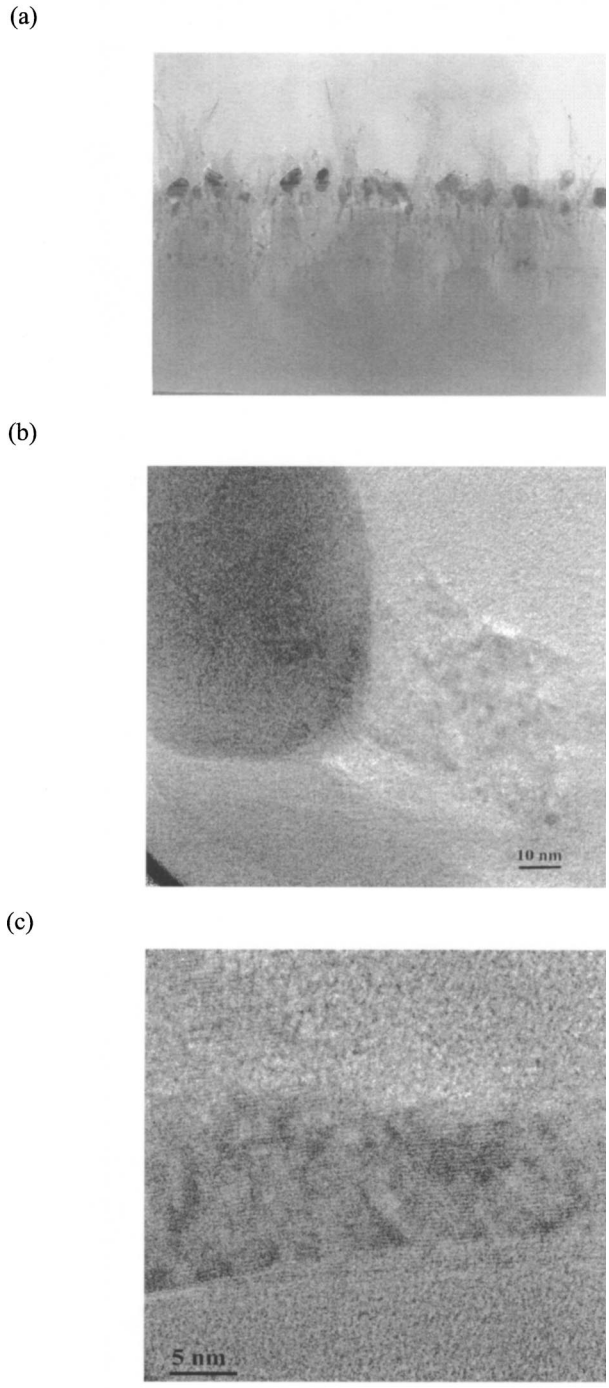

FIG. 2. TEM images of (a) cross-section view, (b) individual of CNTWNCCs, and (c) the lateral section of carbon nanotip.

of the tip. Based on SEM pictures, CNTWNCCs grow up to about 1 μm long and 60 nm in diameter, causing them to exhibit a high aspect ratio, and making them good candidates for the application of field emission.

Figure 2(a) reveals the TEM images of CNTWNCCs. Nanocrystalline chromium carbides are clearly embedded on the top of the carbon nanotips. Incidentally, sparse carbon nanotubes attached to the nanocrystalline chromium carbides are also observed. This is resulted from Cr film playing a catalyst role for the growth of nanotubes.[11] In TEM scope, nanotubes are rare to be seen. Figure 2(a) is intentionally displayed for showing the existence of nanotubes. This explains why there are no nanotubes in Fig. 1(a). Now, we focus on activating the nanocrystalline carbides to make them act as catalysts and templates for the further growth of carbon nanotubes Thus, the field emission application could be significantly improved. Figure 2(b) shows the individual carbon nanotips with nanocrystalline chromium carbide. Unlike hollow carbon nanotubes, Fig. 2(c) shows that the carbon nanotips have a solid structure. Our previous work provides further information about carbon nanotips.[9]

Figure 3(a) shows a TEM image of an individual chromium carbide particle. The high-resolution TEM image depicts nanocrystalline chromium carbide. The diffraction pattern (DP) taken from the chromium carbide in Fig. 3(b) also clearly proves its nanocrystalline structure. Further analysis

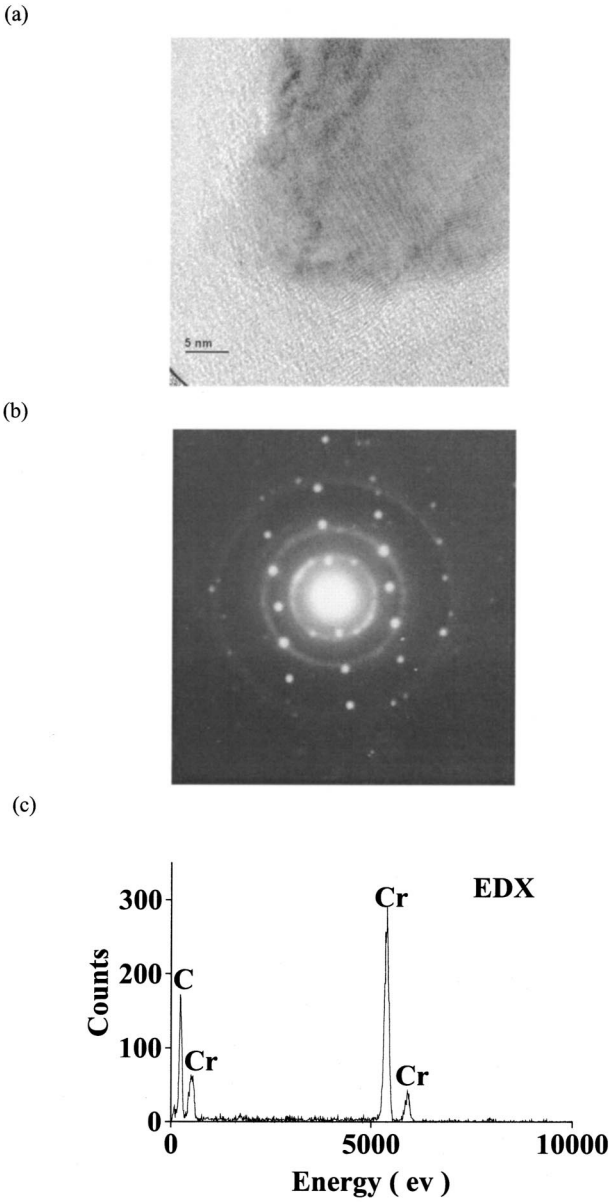

FIG. 3. (a) TEM images, (b) DP, and (c) EDX spectrum of nanocrystalline chromium carbide, respectively.

of chromium carbides is performed by EDX technique. EDX spectrum provides a direct evidence of the chromium and carbon elements in chromium carbide.

The field emission tests are performed on a diode structure, in which CNTWNCCs are separated from the anode, indium tin oxide (ITO) glass, using 500 μm glass as spacers. Green color phosphor coated with 1 cm^2 area on ITO is used to probe the emission image and the emission density. The emission current (I) is measured as a function of the anode-to-cathode voltage in a vacuum of 1×10^{-6} Torr. The Fowler–Nordheim (F–N) theory[12] is the most commonly used model for the emission of cold electrons from a metal under a strong applied field. Figure 4 displays the $I-V$ curve

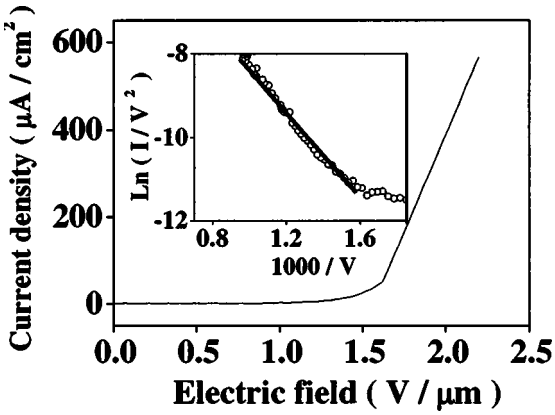

FIG. 4. The current density (J) vs electric field (E) and an inset of F–N plot of CNTWNCCs.

and F–N plot of CNTWNCCs. Plotting Ln (I/V^2) against $1/V$ (F–N plot) should yield a straight line, implying that CNTWNCCs exhibit the property of field emission. A useful parameter for comparison with other field emitters is E_{to} (turn-on field), which is the field V/d (applied voltage/distance between cathode and anode) required to produce a current of 10 $\mu A/cm^2$. The current density, which is 100 $\mu A/cm^2$ as a function of time is further measured to determine the stability of the emitters. Experimental data reveal that the emitted light is brilliant and stable with a fluctuation less than 10% in 1 h. The $I-V$ results clearly show that CNTWNCCs exhibit a favorable field emission property, that is, a turn-on field of 1.38 V/μm and 565 $\mu A/cm^2$ at 2.2 V/μm. It is attributed to the following reasons (i) good alignment and (ii) high aspect ratio of nanotips. Besides, nanocrystalline chromium carbides are also expected to be the improvement in the field emission property. Due to the nanosize effect, the nanoparticles may offer higher electron-supply capability as well as better surface electrical conductivity of the CNTWNCCs as compared to those pure carbon nanotips.

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