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Comparative study on catalyst-free formation and electron field emission of carbon nanotips and nanotubes grown by chemical vapor deposition

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ABSTRACT

The catalyst-free growth of carbon nanotips and nanotubes on silicon substrate pre-deposited with carbon film was realized under different temperatures in plasma-enhanced hot filament chemical vapor deposition system, in which methane, nitrogen and hydrogen were used as the reactive gases. The structure and composition of synthesized carbon nanotips and nanotubes were investigated using field emission scanning electron microscope, transmission electron microscope and micro-Raman spectroscopy, respectively. The results indicate that the carbon nanotips are formed at about 800 °C while the carbon nanotubes are formed about 900 °C. According to the ion bombardment effect and the diffusion at different temperatures, the catalyst-free formation of carbon nanotips and nanotubes was comparatively studied. The transformation from carbon film to spherical carbon particles at a high temperature results in the formation of carbon nanotubes depending on the diffusion of carbon. At a low temperature, the carbon film still locates at the substrate and leads to the formation of carbon nanotips relying on the sputtering-etching of etching ions and the deposition of carbonaceous ions. In addition, the electron field emission characteristics of carbon nanotips and nanotubes were investigated. The results indicate that there is much difference in the electron field emission properties for the carbon nanotips and nanotubes. According to the thermal effect produced by Joule heat during electron emission, the difference was interpreted.

1. Introduction

In last decades, low dimensional carbon-based materials such as carbon nanotubes, polymer nanofibers, carbon nanotips and graphene have attracted much attention due to their novel structures and extensive applications in the areas of nanoelectronic and nanophotonic devices, biology and medicine [1–7]. When the carbon-based carbon nanomaterials are applied, they must be free of metal particles to meet the requirements of some properties. For example, the catalyst particles remaining in carbon nanotubes can result in some detriment effects such as the lowing of thermal stability and the production of toxicity [2]. Thus, the catalyst particles in carbon nanotubes must be removed before applications. But, it is still an intractable problem to remove catalyst particles completely from carbon nanotube specimens [2]. So, Xu et al. believe that the catalyst-free fabrication of nanomaterials is a great challenge nowadays [8], i.e., the catalyst-free synthesis of carbon nanomaterials is significant for their applications.

Reactive plasma is an effective tool to fabricate the carbon nanomaterials [9], therefore we have combined plasma with hot filament chemical vapor deposition system (PEHFCVD) to synthesize the carbon nanotips without catalyst in last years. Recently, we found an interesting experimental phenomenon when we studied the catalyst-free growth of carbon nanotips by PEHFCVD under different conditions, i.e., the carbon nanotips and nanotubes can be grown at low and high temperatures, respectively.

In this work, the catalyst-free formation of carbon nanotips and nanotubes was comparably studied by analyzing the growth conditions and the ion bombardment effect. In addition, the electron field emission (EFE) properties of carbon nanotips and nanotubes were investigated. In this paper, we will report the results on the catalyst-free growth and EFE properties of carbon nanotips and nanotubes.

2. Experimental details

To induce the formation of carbon nanotips and nanotubes, a thin carbon film with a thickness of about 10 nm was deposited on silicon substrate using RF sputtering. During deposition of the

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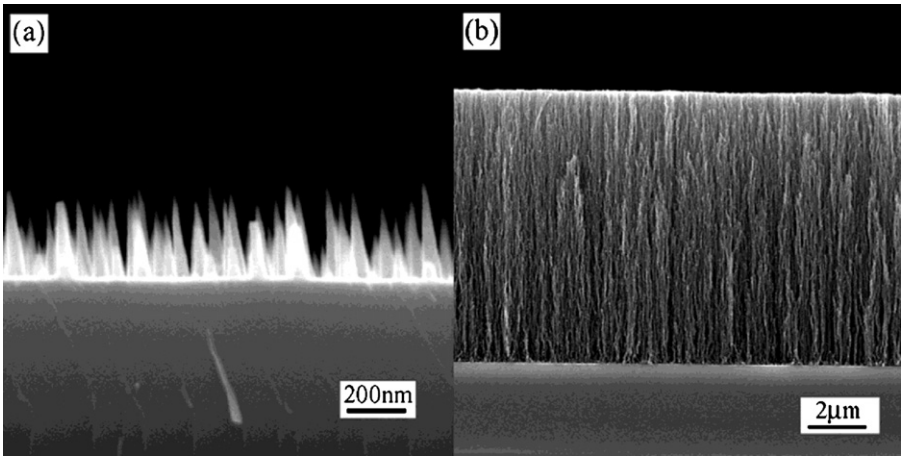

Fig. 1. FESEM images of (a) specimen A and (b) specimen B.

carbon film, the graphite target was sputtered for 5 min by argon ions in a vacuum of 0.5 Pa. The power of RF plasma was 200 W.

The carbon nanotips and nanotubes were synthesized on the silicon substrate pre-deposited with carbon film in PEHFCVD system described in Ref. [4]. Here, the substrate was heated using a heating system composed of three hot tungsten filaments in the CVD system. The short distance of about 8 mm between the substrate and filaments makes the substrate reach the growth temperature quickly. In the growth process of carbon nanotips and nanotubes, methane, hydrogen and nitrogen were used as the working gases and their flow rates were 20, 65 and 15 sccm, respectively. The working pressure was about 2×10^3 Pa. A DC power supply with a constant current was used to produce plasma, where the anode and cathode were connected with the filament electrode and the substrate, respectively. A negative bias relative to the filaments was applied to the substrate through a molybdenum holder. When the carbon nanotips and nanotubes were grown, the bias current was set to 160 mA. The corresponding bias voltage changed from 960 to 1000 V in the growth time of 20 min. During the experiment, the substrate temperature was altered by changing filament current to prepare two specimens A and B at about 800 and 900 °C, respectively.

The structure and composition of synthesized carbon nanomaterials were investigated using S-4800 field emission scanning electron microscope (FESEM), JEOL 2010 transmission electron microscope (TEM) and micro-Raman spectroscopy using the 514 nm line of Ar^+ laser as the excitation source, respectively.

The EFE characteristics of carbon nanomaterials were measured using a diode configuration in a high vacuum of $\sim 10^{-6}$ Pa. In the diode configuration, the carbon nanomaterials and a polished silicon wafer were used as the cathode and anode, respectively (they were separated by glass fiber with a diameter of 80 μm).

3. Results

Fig. 1(a) and (b) are the FESEM images of carbon nanomaterials synthesized at about 800 and 900 °C, respectively. From Fig. 1, one can see that the specimen A is composed of carbon nanotips while the specimen B is composed of carbon nanowires. After the typical carbon nanotips and the nanowires in Fig. 1 were measured using a ruler, the bar length and the value which the bar length represents in Fig. 1 were used to calculate the height, bottom width and tip diameter of carbon nanotips. Then, the error was calculated using the formula of arithmetic mean error. Finally, we obtain the average values of height, bottom width and tip diameter of carbon nanotips and they are about 275 ± 25, 72 ± 8 and 12 ± 5 nm, respectively; the length of carbon nanowires is about 9.3 μm.

To further confirm the structure of carbon nanowires, they were investigated by TEM. Fig. 2 shows the TEM images of carbon nanowires scraped from the specimen B, while the inset in Fig. 2(b) is the electron diffraction pattern. As shown in Fig. 2, the nanowires feature tube structure, but there are some carbon particles on the surface of tubes. This mixing structure is confirmed by the electron diffraction pattern. From the inset, the electron diffraction pattern

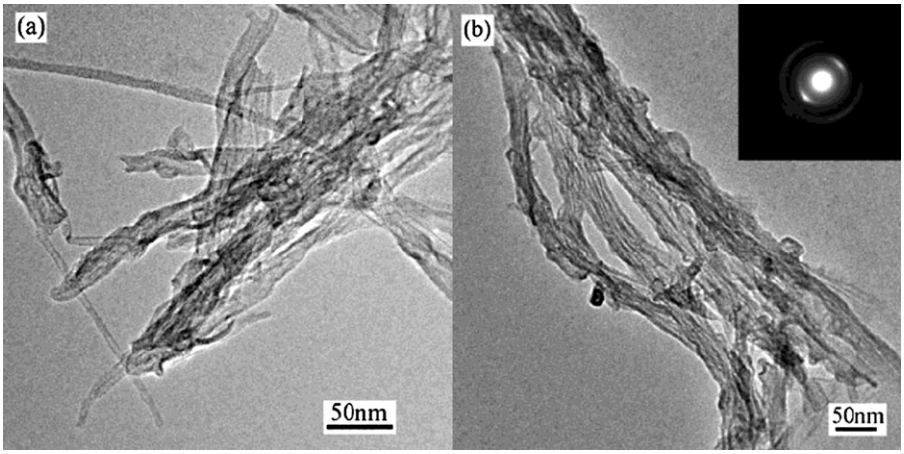

Fig. 2. TEM images of carbon nanotubes (a): including top of carbon nanotubes; (b) containing carbon particles on the surface of carbon nanotubes. The inset is the electron diffraction pattern of a selected area.