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Comparative study of the carbon nanofilm and nanodots grown by plasma-enhanced hot filament chemical vapor deposition

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ABSTRACT

Carbon nanofilm and nanodots were grown by plasma-enhanced hot filament chemical vapor deposition using methane, hydrogen and nitrogen as the reactive gases. The results of field emission scanning electron microscopy, micro-Raman spectroscopy and X-ray photoelectron spectroscopy indicate that the amorphous carbon nanofilm and nanodots are formed without and with nitrogen, respectively. The formation of carbon nanofilm and nanodots is the consequence of different sputtering-etching effects. The photoluminescence (PL) of carbon nanofilm and nanodots was studied in a SPEX 1403 Ramalog system using a 325 nm He–Cd laser as an excitation source and the PL spectra show the PL bands centered at about 411 and 513 nm for the carbon nanofilm and 405 and 504 nm for the carbon nanodots. Simultaneously, the PL results also indicate that the intensity of PL bands of carbon nanofilm is lower than that of carbon nanodots. The generation of different PL bands was interpreted by the transition mechanism. The difference in the intensity of PL bands is related to the size of carbon nanodots. The electron field emission (EFE) characteristics of carbon nanofilm and nanodots were investigated in a high-vacuum system. The results show that Fowler–Nordhelm curves are composed of two or three straight lines and the carbon nanofilm can emit a high current density, which originate from the diversification of carbon nanodots. The difference in the EFE results of carbon nanofilm and nanodots is associated to the size and number of carbon nanodots. These results can enrich our knowledge about carbon-based nanomaterials and are important to fabricate the carbon-based solid nanodevices in the field of optoelectronics.

1. Introduction

Carbon can form different structural materials depending on the sp^1, sp^2 and sp^3 hybridized C–C bonds, thus the carbon-based nanomaterials have been extensively studied in the last decades to meet different applications. For example, graphene, carbon nanotubes, carbon nanotips and nanodots have been synthesized using different methods so that they reveal the potential applications in the fields of microelectronics and optoelectronics [1–6]. In particular, the carbon nanodots can generate strong photoluminescence (PL) and show the excellent photocatalytic

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properties [7–9], which recently attract significant attention. However, the carbon nanofilms can generate the PL [10,11], is there the difference in the PL behaviors of carbon nanofilms and nanodots? If there is the difference, what is the difference? This activates us to comparatively study on the PL properties of carbon nanofilms and nanodots. Simultaneously, the electron field emission (EFE) properties of carbon nanofilms and nanodots are comparatively studied.

Carbon nanodots have been synthesized by various chemical and physical methods such as electrochemical etching of carbon fibers, hydrothermal synthesis and laser ablation [6,9,12,13]. In this work, the carbon nanofilm and carbon nanodots were synthesized by plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) because the reactive plasma is extensively employed to fabricate nanomaterials [14,15]. It is interesting to find that the carbon nanofilm and nanodots were synthesized without and with nitrogen in the reactive gases. When the carbon nanodots were prepared by electrochemical etching and hydrothermal methods, they required a long growth time (above 8 h) and the special treatments such as the stirring, filtering, centrifugation and dry [9,12]. In comparison with the electrochemical etching and hydrothermal methods, the PEHFCVD method simplifies the preparation procedure and lowers the growth time because the carbon nanodots can be directly synthesized for 15 min by PEFCVD.

The PL and EFE properties of carbon nanofilm and nanodots were studied. The results show that the PL bands of carbon nanodots have a blue shift relative to the carbon nanofilm while the carbon nanofilm can emit higher current density relative to the carbon nanodots. Combined with the theory related to sputtering, the formation of carbon nanofilm and nanodots was studied. According to the transition mechanism and the structures of carbon nanofilm and nanodots, the PL and EFE results were analyzed. In this paper, we report the results on the comparative study of formation, structure, photoluminescence and electron field emission of carbon nanofilm and nanodots.

2. Experimental details

The carbon nanofilm and nanodots were synthesized in a PEHFCVD system, which is described in detail in Ref. [16]. Briefly, the reactive chamber includes both the filament and bias systems for the decomposition of reactive gases, the heating of substrate and the production of plasma, respectively. The filament system is constructed by three parallel tungsten filaments, which were heated by AC current to about 1800 °C. The distance between the filaments and substrate was about 8 mm. The temperature of filaments was so high that the silicon substrate was fast heated to above 800 °C because of its exposure to the filaments. In the bias system, a DC power supply with constant current is applied. Both the anode and cathode of DC power supply are connected to the filaments and substrate, respectively, and the cathode is connected to the substrate through a molybdenum holder.

The synthesis process includes the treatment of silicon surface by plasma and the preparation of carbon nanomaterials. Because it is difficult to nucleate on a mirror-polished silicon surface, the silicon substrate was treated by N_2–H_2 plasma to produce the micro-pits on the surface of silicon for lowering the energy required for carbon nucleation [17]. After the silicon substrate was placed into the reactive chamber, the chamber was evacuated to a pressure of lower than 2 Pa. Then, nitrogen and hydrogen gases were inlet into the chamber and the pressure was adjusted to about 2×10^3 Pa. Under this pressure, the filaments were heated to 1800 °C. Simultaneously, the silicon substrate was fast heated to about 850 °C. At this moment, the bias power supply was turned on to produce plasma. The bias current was set to 140 mA to treat the silicon surface for 5 min. After the silicon surface was treated, the bias power supply was turned off and methane was introduced into the chamber. Once the flow rates of reactive gases were adjusted according to the preparation conditions, the bias power supply was turned on again and the bias current was set to 140 mA to deposit the carbon nanomaterials for 15 min. In this work, two specimens A and B were prepared and the preparation parameters are summarized in Table 1. Through experiment, we find that the method has a good reproducibility for the preparation of carbon nanofilms and nanodots and have used the carbon nanofilms and nanodots as the seeds to successfully synthesize the graphene flakes (reported in other papers).

Table 1
The flow rates of CH_4, H_2 and N_2, growth temperature T_s, bias current I_b, bias U_b, and growth time t.

Specimen	CH_4 (sccm)	H_2 (sccm)	N_2 (sccm)	T_s (°C)	I_b (mA)	U_b (V)	t (min)
A	20	80	0	850	140	840–960	15
B	20	50	30	850	140	800–860	15

The morphologies and composition of specimens were investigated by a Hitachi S-4800 field emission scanning electron microscopy (FESEM) (operated at 15 KV), a HR-800 micro-Raman spectroscopy using the 532 nm line of semiconductor laser and a ESCALAB 250 X-ray photoelectron spectroscopy (XPS) using an Al Kα X-ray source, respectively. The PL measurements of specimens were carried out in a SPEX 1403 Ramalog system, where the 325 nm line of He–Cd laser was used as an excitation source.

The EFE characteristics of specimens were studied using a diode configuration in a high-vacuum system of $\sim10^{-5}$ Pa. The cathode and anode of diode configuration were composed of the specimen and a mirror-polished silicon wafer, respectively. Both the electrodes were isolated using the glass fibers with a diameter of 125 μm. During the process of measurement, the voltage was changed from 1 to 980 V.

3. Results and discussion

3.1. Structures and composition of carbon nanofilm and nanodots

Fig. 1 shows the FESEM images of specimens A and B. As shown in Fig. 1, the carbon nanofilm and nanodots were