



Effects of plasma and gas flow conditions on the structures and photoluminescence of carbon nanomaterials

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ABSTRACT

In this work, we demonstrate the conversion of amorphous to crystalline carbon nanomaterials through the synthesis of carbon nanomaterials on silicon substrates coated with gold films in CH₄-N₂-H₂ environment and CH₄-N₂-H₂ plasma by hot filament chemical vapor deposition, respectively. The characterization results indicate that the flow rate of methane and plasma lead to the structural conversion and the change of composition of carbon nanomaterials, which are related to the conversion of hydrocarbon radicals to benzene molecules on the gold nanoparticles and the incorporation of nitrogen in the carbon nanomaterials caused by the plasma. Furthermore, the isothermal absorption theory was applied to study the structural conversion of amorphous to crystalline carbon nanomaterials in the CH₄-N₂-H₂ plasma. The studies suggest that the change of surface tension caused by the dissolution of different carbon species in gold nanoparticles plays a key role for the structural conversion of the carbon nanomaterials. The photoluminescence properties of synthesized carbon nanomaterials were investigated at room temperature. The results exhibit that the carbon nanomaterials can generate the ultraviolet, blue, green and red light due to the functional groups on the surfaces of carbon nanomaterials and they are expected to emit white light after the functional groups are adjusted. The outcomes of this work are significant to control the structures of carbon nanomaterials and contribute the development of white light emission devices.

1. Introduction

In last decades, carbon nanomaterials have attracted much increasing attention due to their structures and properties different from their bulk materials and their enormous contributions to the foundation and application studies [1–6]. To date, the carbon nanomaterials including nanodiamond, carbon nanotips (or cones), and graphene have been successfully synthesized by various methods such as wet chemical method, high pressure high temperature method and chemical vapor deposition method [7–11]. In particular, the carbon nanomaterials are usually synthesized by plasma-enhanced chemical vapor deposition [12–15].

Carbon nanomaterials can be composed of *sp*³ carbon, *sp*² carbon or their mixture to form the diamond, graphene (or graphite) and amorphous structures, respectively [16]. As a result, these carbon structures exhibit tremendous differences in their properties. For example,

nanodiamond is a wide bandgap material [10], while graphene becomes zero bandgap nanomaterial [3] and the bandgap of amorphous carbon depends on the ratio of *sp*² to *sp*³ carbon [17]. Methane, as the main component of natural gas, is an abundant carbon source with a low cost, it is the reason why methane is extensively used to synthesize the carbon nanomaterials by chemical vapor deposition [10,12–14].

Since the carbon nanomaterials are synthesized using the same carbon source by chemical vapor deposition, why are there huge differences in their structures? From the reported results, a low concentration of methane in hydrogen leads to the formation of diamond structure in chemical vapor deposition system [10], while a high concentration of methane in hydrogen and argon synthesizes the graphene structure under plasma [12] and an appropriate concentration of methane in hydrogen and nitrogen results in the growth of nitrogenated amorphous carbon structure under plasma [14]. In other words, the structures and composition of carbon nanomaterials are intimately

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related to the plasma and concentration of methane in the reaction gases.

How do the plasma and methane concentration lead to the structural and compositional changes of carbon nanomaterials? To date, these issues are open questions and have not been understood well although the formation mechanisms of different carbon nanomaterials have been investigated. Due to structure-dependent properties of carbon nanomaterials, it is necessary to study the effects of methane concentration and plasma on the structures and composition of carbon nanomaterials for controlling their structures and composition. During the synthesis of carbon nanomaterials, the concentration of methane in the mixed gases is determined by the flow rate of methane, thus we aim to study the effects of plasma and gas flow conditions on the structural and compositional changes of carbon nanomaterials in this work.

In the previous works, we used plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) and HFCVD to synthesize the amorphous carbon nanorods, graphene films and graphene nanoflakes on the silicon substrates using methane as the carbon source [14,18,19]. In this work, carbon nanomaterials were synthesized through changing the growth conditions compared to the previous works. In particular, we studied the structural and compositional changes of carbon nanomaterials depending on the methane flow rates and plasma, and demonstrate that the conversion of amorphous to crystalline carbon nanomaterials results from the change of surface tension caused by the dissolution of different carbon species in gold nanoparticles and the incorporation of nitrogen in the carbon nanomaterials is related to the ionization of nitrogen.

In the synthesis process of carbon nanomaterials, the process involves the ionization and decomposition of reaction gases, the absorption of hydrocarbon ions and radicals, the reactions of hydrocarbon ions and radicals on the surfaces of gold nanoparticles and the dissolution of reaction products, etc. Beginning with the ionization of methane, the isothermal absorption theory was used to study the structural conversion of carbon nanomaterials, and then the formation of crystalline carbon nanomaterials with and without plasma as well as the incorporation of nitrogen in the carbon nanomaterials were investigated. Considering the application of carbon nanomaterials in the area of optoelectronics, their photoluminescence (PL) properties were studied.

2. Experimental details

The synthesis of carbon nanomaterials was carried out in the PEHFCVD system, which is described in detail elsewhere [20]. Briefly, three tungsten filaments in the CVD chamber are used to decompose the reaction gases and heat the substrate. The substrate is installed on a molybdenum holder, which locates below the filaments about 10 mm. A DC power supply is used to produce the plasma, where the positive electrode is connected with the filaments and the negative electrode is connected with molybdenum holder, respectively. To make the filaments work stably, the tungsten filaments were carbonized in the mixture of 5 sccm CH₄ and 95 sccm H₂ for ~3 h at about 1800 °C.

Before the carbon nanomaterials were synthesized, the silicon substrate was chemically cleaned as the procedure described in Ref. [20]. Because it is difficult for these materials to nucleate and grow on a polished silicon substrate [21], the silicon substrate must be further treated. In the previous work, the silicon substrate was treated in N₂-H₂ plasma [18], here a gold film with a thickness of ~5 nm was deposited on the cleaned silicon substrate by magnetic sputtering.

In the synthesis process of carbon nanomaterials, methane, nitrogen and hydrogen were used as the reaction gases. To avoid the absorption of methane on the gold nanoparticles during heating the substrate, nitrogen and hydrogen were inlet into the CVD chamber after the base pressure in the CVD chamber was below 2 Pa, and then the pressure in the CVD chamber was adjusted and stabilized at $\sim 2 \times 10^3$ Pa through the vacuum valve. After the filaments were heated, methane was inlet into

Table 1
The synthesis conditions of carbon nanomaterials.

Sample	CH ₄ (sccm)	H ₂ (sccm)	N ₂ (sccm)	Bias current (mA)	Bias (V)	Growth time(min)
A	20	40	40	—	—	20
B	50	25	25	—	—	10
C	20	40	40	160	~880–900	20
D	20	40	40	160	~880–900	25
E	50	25	25	160	~900	10
F	50	25	25	160	~900	20

the chamber. Due to a short distance of the substrate from the filaments, the substrate was fast heated to 850 °C in a high heating rate of ~275 °C/min. In this case, the carbon nanomaterials started to be synthesized in the CH₄-N₂-H₂ environment and CH₄-N₂-H₂ plasma, respectively. The detail synthesis conditions are given in Table 1. During the synthesis of carbon nanomaterials, the bias gradually increases due to the change of filaments and secondary electron emission from the grown carbon nanomaterials, which is given Table 1.

The morphologies, structures and composition of synthesized carbon nanomaterials were characterized by S-4800 field emission scanning electron microscope (FESEM), JEOL 2010F and Titan G² transmission electron microscope (TEM), HR 800 micro-Raman spectroscopy using 532 nm line of semiconductor laser and ESCALAB 250 X-ray photoelectron spectroscopy (XPS) using Al K α X-ray source. The room temperature photoluminescence of carbon nanomaterials was measured in Horiba Scientific LabRAM HR evolution Raman spectrometer under the excitation of 325 nm line of He-Cd laser. During measurement, the power of laser was set to 6.8 mW and the diameter of the light spot was about 2 μ m.

3. Results and discussion

3.1. Structures and composition of synthesized nanomaterials

Fig. 1(a)–(f) are the FESEM images of carbon nanomaterials synthesized using the conditions shown in Table 1. From Fig. 1, one can apparently see that the samples A and B are composed of carbon nanosheets, the samples C and D are the carbon nanorod structure, and the sample E and F are the films composed of carbon nanosheets.

Furthermore, the areas marked by red dot rings in Fig. 1(c) and (d) show the gold nanoparticles on the tops of nanorods, which indicate that the carbon nanorods grow in a mode of gas-liquid-solid. Fig. 1 indicates that the plasma and methane flow rate have huge influences on the structures of carbon nanomaterials.

Fig. 2(a)–(c) are the Raman spectra of samples A–F. As shown in Fig. 2(a), the Raman spectra of samples A and B show the D, G and 2D peaks of graphene structure at about 1353, 1586 and 2700 cm⁻¹, respectively [22,23]. The peaks at 2941 cm⁻¹ in Fig. 2(a) are the D + G peaks of graphene nanosheets [22]. In Fig. 2(b) and (c), every Raman spectra shows the D and G peaks at about 1353 and 1592 cm⁻¹ of carbon [14,22,23], while the Raman spectra of samples E and F also show the 2D peaks at about 2700 cm⁻¹ of graphene structure [22,23]. In addition, Fig. 2(c) shows the D + G peaks of carbon at about 2930 cm⁻¹ [22]. In Fig. 2(a), the strong D peaks indicate the graphene nanosheets contain amorphous phase. Fig. 2(b) obviously show that the D peaks of samples C and D are stronger than the G peaks, thus the carbon nanorods are amorphous structure [24]. In Fig. 2(c), the 2D peak at about 2700 cm⁻¹ indicates that the samples E and F are graphene structure [22,23], why do their Raman spectra show the stronger D peaks than G peaks? In Raman spectrum, the appearance of 2D peak at ~2700 cm⁻¹ indicates the formation of graphene structure, but the D peak is related to the edges of graphene [25]. As shown in Fig. 1(e) and (f), the samples E and F are composed of a number of carbon sheets, this

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