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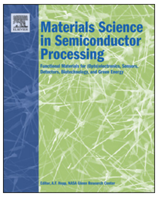

Growth, photoluminescence and thermal conductance of graphene-like nanoflakes grown on copper foils in methane environment

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ABSTRACT

In this paper, we reported a simple and effective synthesis method of graphene-like nanoflakes (GNFs) on the copper foils by hot filament chemical vapor deposition in methane environment. The structure and composition of GNFs were studied by field emission scanning electron microscope, micro-Raman spectroscope, and Fourier transform infrared spectroscope, respectively. According to the characterization results and the growth process, the formation mechanism of GNFs was investigated, which was based on the formation of carbon particles and the diffusion and assembly of carbon atoms. The photoluminescence (PL) of GNFs was measured in a Ramalog system and the PL spectra show a weak and a strong PL bands centered at about 411 and 515 nm, respectively. The measurement results of thermal conductance of GNFs indicate that the thermal conductivity of GNFs is up to 480 W/mK. Our results can enrich the knowledge on the synthesis, optical and thermal properties of graphene-based nanomaterials and contribute to the development of graphene-based devices.

1. Introduction

Recently, low-dimensional carbon-based nanomaterials such as graphene, carbon nanotubes, nanodots and silicon carbide nanofilms have received much attention due to their unique structures and properties [1–4]. For the graphene and graphene nanoribbons, they have fascinating physical properties such as quantum electronic transport, a tunable band gap, giant intrinsic mobility, high elasticity and electromechanical modulation [5–7]. The graphene nanoflakes (GNFs) are composed of multilayer graphene nanosheets, which have similar structure of graphene and graphene nanoribbons. In particular, the GNFs can vertically grow and form the thin graphitic edge planes. The results of Shang et al. indicate that the thin graphitic edge planes are basically responsible for the electrocatalytic and biosensing properties, which imply that the GNFs have extensively potential applications in the areas of electrochemistry and biology such as the fabrication of electrodes of electrocatalytic and biosensing devices [8]. Moreover, the GNF films can form graphene network [7], thus they can be used to fabricate the pressure sensors because the strain response of graphene network mainly depends on the overlap area and contact resistance of neighboring graphene sheets [9].

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This is the possible reason that the GNFs have become the spotlight of extensive research effort. Since the reactive plasma was extensively used to fabricate various nanomaterials [10,11], the GNFs were synthesized by plasma-enhanced chemical vapor deposition and magnetically-enhanced arc discharge [7,12]. The properties of GNFs are related to the layer number of graphene and their stacking-assembly order [7], which activates us to synthesize the GNFs using different methods and study their properties. When the graphene is synthesized by chemical vapor deposition (CVD), a mixture of methane and hydrogen is usually employed [1,5,7]. However, the atomic hydrogen can etch the graphite carbon [13,14], thus the GNFs were grown using methane as the reactive gas in this work to reduce the etching effect of hydrogen on the GNFs. Since copper can catalyze the growth of carbon-based materials such as graphite, carbon nanotubes and graphene [15], we used the copper foils as the substrate to grow the GNFs in hot filament chemical vapor deposition (HFCVD) system. To date, the CVD growth of graphene on copper foils has been extensively studied [1,14,16,17]. For the formation of graphene on copper surface, it is accepted that the formation of graphene on copper surface results from the surface reactions and that the hydrogen-assisted dehydrogenation of hydrocarbon is responsible for the formation of graphene [14,16,17]. However, can graphene be formed on copper surface in methane environment? It is found that the amorphous carbon and GNFs are formed depending on the growth time in the methane environment in this work.

The perfect graphene lacks a bandgap so that it is difficult to generate photoluminescence (PL) [18], while the graphene oxide with the bandgap generates blue light [19]. Simultaneously, the results of Han et al. indicate that the graphene nanoribbons possess the electronic bandgap [6]. Because of the structural similarity between the GNFs and graphene nanoribbons, the GNFs should have a bandgap and generate the PL, thus the PL properties of GNFs were studied. In addition, the suspended graphene has a very high thermal conductivity of 5300 W/mK near 350 K [20] so that we were interested in the thermal properties of GNFs and also studied their thermal conductivity.

2. Experimental

To grow the GNFs, the surfaces of copper foils were polished with SiC paper to remove the impurities, and then the foils were cleaned in the ultrasonic solution of ethanol for 15 min.

The GNFs were synthesized on copper foils in HFCVD system described in Ref. [21]. Briefly, the CVD chamber in the HFCVD system contains a heating system constructed by three tungsten filaments which were heated to about 1800 °C. The distance between the filaments and copper foils was about 8 mm. Since the copper foils were exposed to the filaments, the copper foils were fast heated to above 850 °C by the hot filaments. After the chamber was evacuated to lower than 2 Pa, hydrogen with a flow rate of 50 sccm was inlet into the CVD chamber, and then the pressure was adjusted to about 2×10^3 Pa. Simultaneously, the filaments were heated by AC current in hydrogen environment. Once the temperature of a copper foil reached about 850 °C, methane was substituted for hydrogen in the same flow rate as hydrogen to synthesize the GNFs. In this work, three specimens were prepared for different growth time. It is found that a lot of GNFs are formed in 10 and 15 min while the amorphous carbon is formed when the growth time is 5 min.

The morphologies of GNFs were investigated using a Hitachi S-4800 field emission scanning electron microscope (FESEM), which was operated at 15 kV. The composition of GNFs was determined by a T64000 micro-Raman spectroscopy using a 514 nm line of Ar^+ laser and a 8400S Shimadzu Fourier transform infrared (FTIR) spectroscopy, respectively.

The PL spectra of GNFs were recorded in a SPEX 1403 Ramalog system using a 325 nm He–Cd laser as an excitation source. The thermal conductivity of GNFs was measured in a LTI-237CM system using the laser-flash method. During the measurement, an Nd: YAG laser was employed, and the excitation wavelength, pulse energy and duration are 10.6 μm, 75 mJ and 10 ns, respectively.

3. Results and discussion

3.1. Structure and composition of GNFs on copper foils

Fig. 1 is the FESEM image and Raman spectrum of specimen grown for 5 min (the Raman spectrum is obtained from HR 800 micro-Raman spectroscopy using the 325 nm line of semiconductor laser). From Fig. 1(a), one can see that the carbon particles are formed and few GNFs are formed. The Raman spectrum in Fig. 1(b) shows that the D, G and 2D peaks of carbon materials are located at about 1349, 1589 and 2705 cm^{-1}, respectively [7]. The very weak 2D peak relative to the G peak indicates that the specimen is composed of amorphous carbon particles.

Fig. 2 is the FESEM images of specimens with the growth time of 10 and 15 min (the specimens are named as A and B), respectively. As shown in Fig. 2, the vertical GNFs are grown on the copper foils. From Fig. 2, one can see that the area of GNFs is increased with the increase of the growth time.

Fig. 3 is the Raman spectra of specimens A and B. In Fig. 3, both the Raman spectra show that the D, G and 2D peaks are located at about 1349, 1583 and 2699 cm^{-1}, respectively. The strong 2D peaks indicate that the GNFs are composed of multi-layer graphene sheets [1,22,23] The weak peak at about 2938 cm^{-1} is attributed to the D+G peak [7]. As shown in Fig. 3, the D peaks for two specimens are strong and the strong D peak of GNFs is observed in Ref. [7]. For the perfect graphene films, the D peak is very weak [1,24] and it mainly results from the edge defects of graphene films [23]. Our specimens are composed of the vertical GNFs so that the edge defects can be detected by Raman spectroscopy, thus the strong D peaks appear in the Raman spectra. Simultaneously, the strong D peak in Ref. [7] is due to the edge defects of GNFs. According to Fig. 3, the intensity ratio of 2D to G peaks is about 0.9 and 0.5 for the spectra (1) and (2), which means that the GNFs of specimen A are thinner than that of specimen B because