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Formation and electron field emission of graphene films grown by hot filament chemical vapor deposition

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HIGHLIGHTS

- Graphene films are grown on gold films by hot filament chemical vapor deposition.
- Hierarchical nanoflower structures made of graphene flakes are demonstrated.
- The size of gold nanodroplets plays an important role in graphene flake formation.
- The films show competitive electron field emission properties.

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ABSTRACT

Graphene films with different structures were catalytically grown on the silicon substrate pre-deposited with a gold film by hot filament chemical vapor deposition under different conditions, where methane, hydrogen and nitrogen were used as the reactive gases. The morphological and compositional properties of graphene films were studied using advanced instruments including field emission scanning electron microscopy, micro-Raman spectroscopy and X-ray photoelectron spectroscopy. The results indicate that the structure and composition of graphene films are changed with the variation of the growth conditions. According to the theory related to thermodynamics, the formation of graphene films was theoretically analyzed and the results indicate that the formation of graphene films is related to the fast incorporation and precipitation of carbon. The electron field emission (EFE) properties of graphene films were studied in a high vacuum system of $\sim 10^{-6}$ Pa and the EFE results show that the turn-on field is in a range of 5.2–5.64 V μm^{-1} and the maximum current density is about 63 μ A cm^{-2} at the field of 7.7 V μm^{-1}. These results are important to control the structure of graphene films and have the potential applications of graphene in various nanodevices.

1. Introduction

Graphene-based nanomaterials have attracted much attention due to their fascinating structural and physical properties such as quantum electronic transport, a tunable band gap, giant intrinsic mobility, high elasticity and electromechanical modulation [1,2]. These properties strongly depend on the number of graphene layers and their stacking-assembly order [3], and thus it is important to study on their growth for their applications.

Since Novoselov et al. discovered graphene in 2004 [4], the synthesis of graphene becomes interesting. Large-area graphene has been successfully synthesized by various methods including chemical and physical methods. For example, the graphene films have been obtained by the solution method and chemical vapor deposition (CVD) method, respectively [5,6]. In particular, the graphene films were extensively synthesized on nickel, copper and gold foils or thick nickel films by CVD [2,7–9]. For the formation of graphene, Kim et al. and Yu et al. believed that it originated from the precipitation of carbon from nickel under fast cooling rate [2,7], while Li et al. suggested that graphene was grown through a surface-catalyzed process due to very low solubility in copper [8]

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and Oznuluer et al. believed that the formation of graphene on gold foil is similar with copper [9]. A typical thickness of copper and gold foils is ~25 μm while for nickel foils it can be up to 0.5 mm [2,7–9]. It is well known that the cost of nickel, copper and gold foils is relatively high. To lower the cost, it is worthwhile to use noble metal films (several tens of nanometers) for the preparation of graphene films. Is it possible to grow graphene films using thin noble metal films? If the graphene films can be formed, is the formation mechanism similar with the noble metal foils? This inspires us to study on the synthesis of graphene films using thin gold films.

In this work, we prepared the graphene films on the silicon substrate pre-deposited with a gold film by hot filament CVD (HFCVD) under different experimental conditions. The morphology, structure and elemental composition of the synthesized graphene films were investigated by advanced instruments including field emission scanning electron microscopy, micro-Raman spectroscopy and X-ray photoelectron spectroscopy. According to the characterization results, the formation of graphene was theoretically analyzed by the theory related to thermodynamics. In addition, the electron field emission (EFE) of graphene films was studied in a high-vacuum system of $\sim 10^{-6}$ Pa and the EFE properties were analyzed by Fowler–Nordhelm (F–N) theory.

2. Experimental details

Due to the large lattice mismatch between graphite ($a_0 = 0.335$ nm) and silicon ($a_0 = 0.543$ nm) [10,11], it is difficult for graphene to nucleate on the mirror-polished silicon surface [11]. In order to grow graphene films, a gold film with about 20 nm thickness was deposited on the silicon substrate using a SBC-12 micro-ion-sputtering system.

The graphene films were grown in a hot filament chemical vapor deposition (HFCVD) system described in Ref. [12]. In the HFCVD system, three coiled tungsten filaments in a parallel arrangement were heated to about 2000 °C for the homogeneous heating of substrate and the decomposition of reactive gases. The substrate was the silicon wafer pre-deposited with a gold film, and was fast heated by the filaments to about 930 °C due to the short distance of about 8 mm between the substrate and the filaments. When the basic pressure in the reactive chamber was below 2 Pa, 100 sccm of hydrogen was inlet into the chamber and the pressure in the chamber was adjusted to about 2×10^3 Pa. Then, the filaments were heated by AC current to about 2000 °C. Once the substrate temperature reached about 930 °C, methane and nitrogen gases were quickly introduced into the chamber and the flow rates of reactive gases were adjusted to grow the graphene films. In this work, three specimens were prepared and the growth conditions were summarized in Table 1.

The structure and composition of carbon films were investigated by S-4800 field emission scanning electron microcopy (FEESEM), HR 800 micro-Raman spectroscopy and ESCALAB 250 X-ray photoelectron spectroscopy (XPS), respectively. During the measurement of the structure of graphene films by FESEM, a high voltage of 15 KV was employed. In the process of Raman measurement, a semiconductor laser at 532 nm line was used as the excitation source. When the graphene films were analyzed by XPS, the Al $K\alpha$ X-ray source was employed.

The EFE measurement of graphene films was carried out in a high-vacuum system of $\sim 10^{-6}$ Pa, in which a diode configuration was employed. In the diode configuration, the specimen was used as the cathode and a mirror-polished silicon wafer was used as the anode, and they were separated by glass fibers with a diameter of 125 μm. During the process of measurement, the voltage was changed from 1 to 900 V.

Table 1
The preparation conditions including the flow rate of gas, temperature T_s and growth time t.

Specimens	CH_4(sccm)	H_2(sccm)	N_2(sccm)	T_s(°C)	t(min)
A	70	0	0	938–929	5
B	70	30	0	923–928	5
C	70	0	30	939–931	5

3. Results and discussion

3.1. Structure and composition of graphene films

Fig. 1 shows the FESEM images of silicon substrate deposited with gold film and the melting of gold film deposited on silicon substrate after heating to 700 °C in hydrogen environment. As shown in Fig. 1(a), the thickness of gold film is about 20 nm. Fig. 1(b) indicates that the gold particles are formed during heating the substrate.

Fig. 2 shows a set of typical low- and high-magnification images for all the three samples A, B, and C. Fig. 2(a)–(c) shows the low-magnification FESEM images of specimens A–C, while Fig. 2(d)–(f) are the high-magnification FESEM images of specimens A–C, respectively. From Fig. 2(a)–(c), one can see that the nanoflower formation is quite non-uniform over the substrate surfaces and they are not formed on the large gold particles. The high-magnification FESEM images in Fig. 2(e)–(f) indicate that the nanoflowers are composed of graphene flakes; this conclusion is also confirmed by the Raman spectra analysis.

To confirm the relationship between graphene films and gold particles, the specimen A was mapped using energy dispersive X-ray spectroscopy and the results are shown in Fig. 3. As shown in Fig. 3, the gold particles are below the graphene films and the graphene sheets are mainly aggregated on and near the gold particles, which indicate that the graphene is grown depending on the gold particles. According to Fig. 3(c), the size of gold particles is in a range of 40–60 nm.

Fig. 4 is the Raman spectra of specimens A–C. As shown in Fig. 4, every spectrum shows five main Raman peaks at 1347, 1586, 1625, 2696, and 2942 cm^{-1}, which are the D, G, D′, 2D, and D + G, respectively [10,13,14]. The D peak is due to the breath modes of sp^2 carbon atoms, which is related to edges of graphene sheets [15]. The G peak originates from the in-plane stretching vibration mode (E_{2g}) of a hexagonal carbon [3]. The 2D peak is the second order of the D peak because the frequency of 2D peak is twice the frequency of D peak [15]. The D′ peak results from an intravalley process [14]. The D + G peak is the combination of D and G peaks due to the disorder [10]. As shown in Fig. 4, the 2D peak in every Raman spectrum is sharp and single, which indicates that the synthesized carbon materials are graphene [15]. The intensity ratio of 2D to G peak can be used to estimate the number of graphene layers [8,15]. According to Fig. 4, the intensity of D, G and 2D peaks and the ratios of 2D to G peak and G to D peak are obtained, and they are given in Table 2. The data in Table 2 indicate that the synthesized carbon materials are composed of multi-layer graphene because the intensity ratio of 2D to G peak for monolayer graphene is about 2 [8]. Simultaneously, the data indicate that the number of graphene layers for the specimens A–C is increased in turn because the intensity ratio of 2D to G peak is gradually reduced with the increase in the number of graphene layers [8].

Fig. 5 is the XPS spectra of specimens A–C. As shown in Fig. 5, every XPS spectrum shows the peaks at the binding energy (BE) of 99.8, 152.5, 284.8, 532.8, and 979.7 eV, which are attributed to Si 2p, Si 2s, C 1s, O 1s, and C KLL, respectively [16].