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Synthesis of graphene on a Ni film by radio-frequency plasma-enhanced chemical vapor deposition

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Large-area single- or multilayer graphene of high quality is synthesized on Ni films by radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) at a relatively low temperature (650°C). In the deposition process, a trace amount of CH_4 gas (2–8 sccm (sccm denotes standard cubic centimeter per minute at STP)) is introduced into the PECVD chamber and only a short deposition time (30–60 s) is used. Single- or multilayer graphene is obtained because carbon atoms from the discharging CH_4 diffuse into the Ni film and then segregate out at its surface. The layer number of the obtained graphene increases when the deposition time or CH_4 gas flow rate is increased. This investigation shows that PECVD is a simple, low-cost, and effective technique to synthesize large-area single- or multilayer graphene, which has potential for application as electronic devices.

graphene, PECVD, large-area

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Graphene is a two-dimensional crystalline sheet of carbon atoms packed into a honeycomb lattice that possesses a wealth of fascinating physical properties such as extremely high thermal conductivity, excellent transparency, tunable band gap, and high chemical and thermal stability [1–10]. In particular, graphene exhibits quantum electronic transport properties and extremely high mobility (about 15000 $cm^2\ V^{-1}\ s^{-1}$) at room temperature, which is much higher than most conventional semiconductor materials [1–5]. Recently, much progress has been achieved in the fabrication of single- or multilayer graphene for use in nanoscale electronic applications including high-speed field-effect transistors, transparent electrodes, ultrasensitive sensors and electromechanical resonators [5–10].

For the purpose of electronic application, the synthesis of low-cost, large-area single- or multilayer graphene is highly desirable [4,11]. However, large-area graphene is difficult to obtain using adhesive tape, mechanical cleavage and chemical exfoliation [12–14]. It has been reported that large-area graphene can be grown epitaxially on single crystal SiC, but SiC substrates are expensive and it is difficult to exfoliate or transfer the graphene from SiC to another substrate because of the strong cohesive strength of the graphene/SiC interface and the extreme chemical stability of SiC [14–17]. Many researchers have reported the direct synthesis of large-area single- or multilayer graphene on transition metal substrates by chemical vapor deposition (CVD) [17–22]. An advantage of CVD is that graphene can be transferred to other substrates because some transition metals can be etched by acid solution [17,18]. However, the deposition temperatures required for thermal CVD are generally higher than 800°C, and a relatively long deposition time is needed. The relatively high deposition temperature stems from the thermal decomposition of hydrocarbons. Therefore, it remains a challenge to develop a simple, effective and reproducible method to synthesize low-cost, high-

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quality and large-area graphene at relatively low temperature.

Recently, some researchers reported the synthesis of high-quality large-area graphene using plasma-enhanced CVD (PECVD) at relatively low temperature. PECVD is probably the most promising method to produce graphene to date because it allows high-quality large-area graphene to be fabricated at low cost [14,23–25]. Also, graphene grown by PECVD exhibits a high carrier mobility, low sheet resistance and high optical transparency, suggesting it is of high quality and has great potential for various applications [14,23–25]. However, because the growth of graphene by PECVD is a recent development, further systematic research is required. In particular, the systematic study of the growth conditions required to produce different layers of graphene is limited. For example, the effects of deposition time and flow of reactive CH_4 gas used during PECVD on the growth of graphene are not well understood.

In this work, we demonstrate that radio-frequency PECVD (RF-PECVD) can be used to synthesize high-quality, large-area single- or multilayer graphene on Ni films at a relatively low temperature of around 650°C, and also explore the effect of deposition time and flow of reactive CH_4 gas on the growth of graphene.

1 Experimental

A Ni film with a thickness of about 150 nm was deposited on a thermally-oxidized Si substrate using direct-current magnetron sputtering. The as-deposited Ni film was placed in the chamber of a PECVD system, and the pressure of the chamber was reduced to 5 Pa. The Ni film was treated at 650°C for 40 min under H_2 gas at a pressure of 200 Pa. Graphene was synthesized on the Ni film using RF-PECVD at a frequency of 13.56 MHz and substrate temperature of 650°C in a mixture of CH_4, Ar and H_2 gases (the gas flow was kept at 2–8, 80, and 40 sccm for CH_4, Ar, and H_2, respectively). The total gas pressure was fixed at 1000 Pa by adjusting the gas outlet valve, and the power was 200 W. The deposition time was 30–60 s. After deposition, the sample was rapidly cooled to room temperature at a cooling rate of about 10°C/s by turning off the heater and filling the chamber with a flow of argon to promote carbon segregation and graphene formation [15,17].

The obtained graphene samples were characterized by Raman spectroscopy (Renishaw Invia, Renshaw, UK) using an excitation wavelength of 514 nm and transmission electron microscopy (TEM, JEOL TEM-2010, JEOL, Japan) operating at 200 kV.

2 Results and discussion

Figure 1 shows the graphene sample synthesized by deposition for 30 s (the ratio of gas flow rates was kept at $CH_4/Ar/H_2$= 2/80/40 sccm). The graphene sample was obtained from floats on the surface of the $FeCl_3$ solution following separation from the Ni film by wet etching in $FeCl_3$ solution (1 mol/L) [8,15]. In the transfer process, the size and shape of the centimeter-scale graphene sample remains basically unchanged, as can be seen by comparing the image in Figure 1 to that in the inset of Figure 1. It is obvious that the size of the obtained graphene is dependent on the surface area of the Ni film, and that the graphene sample can easily be transferred to another substrate for the further evaluation and various applications [4,15].

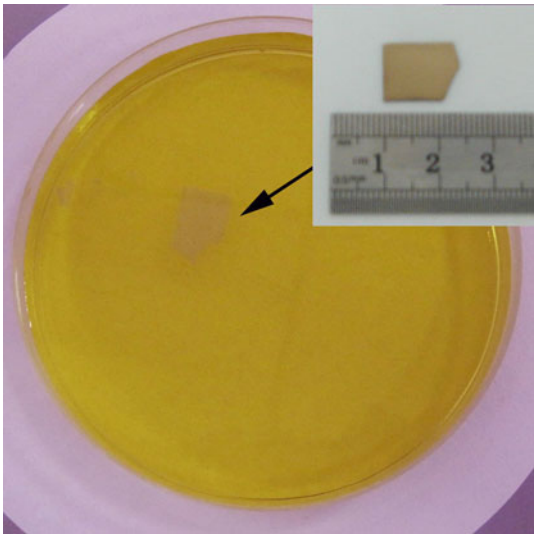

Figure 1 (Color online) A floating graphene sample obtained after etching the Ni layer in 1 mol/L $FeCl_3$ aqueous solution, in which the inset shows the centimeter-scale graphene grown on the $Ni/SiO_2/Si$ substrate. This graphene sample was synthesized with a deposition time of 30 s.

Raman spectra for graphene sample synthesized using various deposition times (the gas flow rate ratio was kept at $CH_4/Ar/H_2$=2/80/40 sccm) are presented in Figure 2. Raman spectroscopy is a powerful technique to characterize the crystalline quality and number of layers in a graphene sample [25]. The most notable feature for graphene is the appearance of the 2D peak, the position and shape of which are related to the formation and the layer number [15,16,25–28]. The graphene formed after deposition for 30 s exhibits a symmetric 2D peak at ~2680 cm^{-1} with a full width at half-maximum of about 33 cm^{-1}, which indicates that it is single-layer graphene [15,16,25–28]. As the deposition time is increased, the positions of the D and G peaks do not shift, but that of the 2D peak shifts obviously. The 2D peaks for the graphene samples grown in 40, 50 and 60 s appear around 2700, 2706 and 2713 cm^{-1}, respectively. The reduced intensity of the 2D peak compared to G peak as the deposition time increases, suggests that the number of graphene layers increases with deposition time. Generally, the intensity ratio of the D peak to the G peak, denoted as the *R*-value, represents the amorphous phase content or the degree

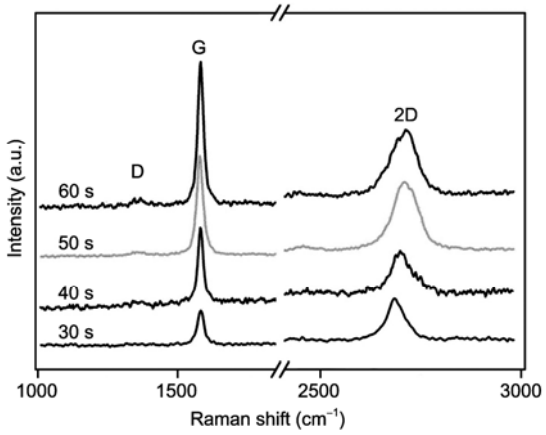

Figure 2 Raman spectra for graphene samples synthesized after various deposition times (the gas flow rate ratio was kept at $CH_4/Ar/H_2$=2/80/40 sccm).

of crystallinity of carbonaceous materials. The smaller the *R*-value, the higher the degree of graphitization (or the fewer crystal defects present). The ratio of the high-intensity G peak at 1580 cm^{-1} to the low-intensity D peak at 1350 cm^{-1} results in a very low *R*-value, which indicates that these graphene samples are of high quality with a high degree of graphitization and low number of crystal defects.

Figure 3(a) displays a TEM image of the graphene sample synthesized by deposition for 30 s. The surface and edge of the obtained graphene are smooth. The selected area electron diffraction (SAED) pattern (inset of Figure 3(a)) corresponding to the square area in Figure 3(a) exhibits clear diffraction spots similar to those from mechanically cleaved graphene [26,29], indicating a graphite lattice structure with a good crystallinity. High resolution TEM (HRTEM) examination of the graphene sample confirms that the change in thickness corresponds to a few graphene layers. The HRTEM image in Figure 3(b) shows that a perfect single-layer graphene grew on the Ni film by deposition for 30 s, which agrees well with Raman and SAED results. The HRTEM images in Figure 3(b) to (e) clearly show that the number of graphene layers increases with increasing deposition time. From the above results, it can be concluded that the deposition time significantly influences the number of graphene layers.

Raman spectra for the graphene samples synthesized using different ratios of gas flow rate at a constant deposition time of 30 s and temperature of 650°C are shown in Figure 4. The Raman spectra for the graphene samples deposited using CH_4 flow rates of 2, 4, 6 and 8 sccm show that the graphene sample contain approximately one layer (1 L), three layers (3 L), five layers (5 L) and ten layers (10 L), respectively, indicating that the number of graphene layers increases with increasing CH_4 gas flow rate. In the syntheses of carbon materials such as nanotubes and nanosheets by PECVD, the ratio of gas flow rate significantly affects the morphology and microstructure of the carbon nano-

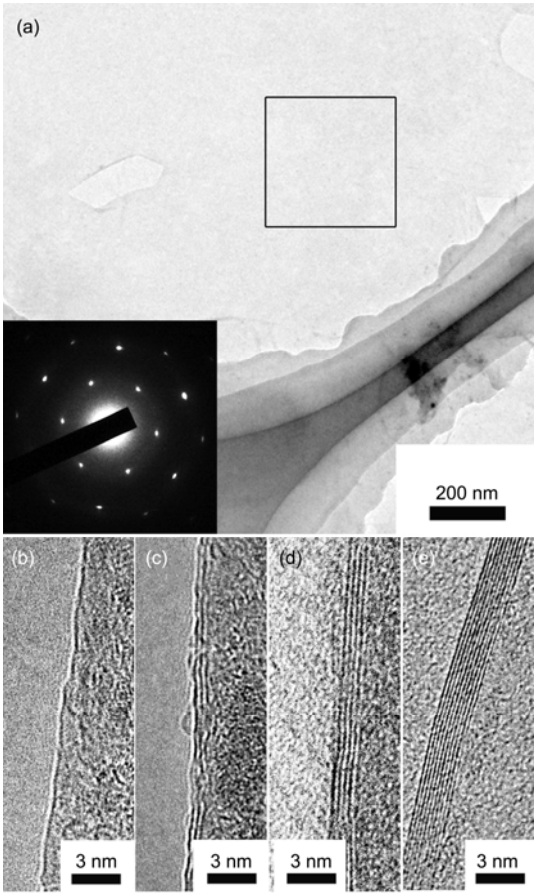

Figure 3 (a) A typical TEM image for the graphene sample grown in 30 s, in which the inset shows the SAED pattern for the sample. HRTEM images of graphene samples synthesized using various deposition times: (b) 30, (c) 40, (d) 50 and (e) 60 s.

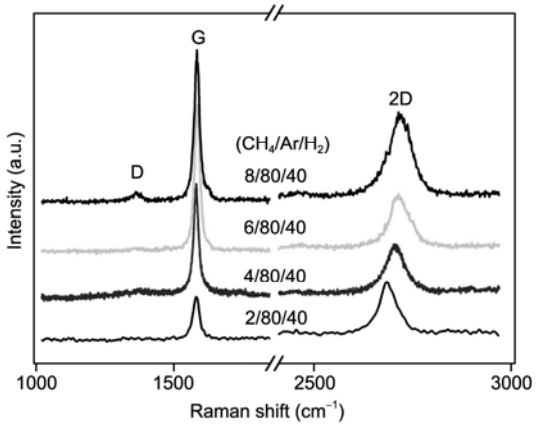

Figure 4 Raman spectra for graphene samples synthesized using various gas flow rate ratios (deposition time: 30 s and temperature: 650°C).

material, and especially, the concentration of carbon source gas is important [25,30,31]. In Figure 4, the two Raman peaks of the highest intensity are the G band at ~1580 cm^{-1} and 2D band at 2680 to 2718 cm^{-1}, while the D band at ~1350 cm^{-1} is very weak. The 2D peak in the Raman spectrum

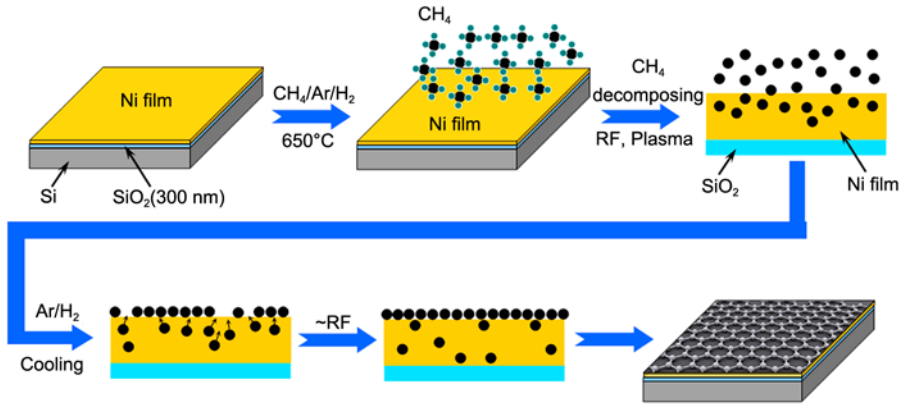

Figure 5 (Color online) Schematic illustration of the formation process of graphene.

for the samples deposited using a CH_4 gas flow rate of 2, 4, 6 and 8 sccm, appears around 2680, 2705, 2712 and 2719 cm^{-1}, respectively. According to previous reports and our above description, the obtained graphene layer deposited using a CH_4 gas flow rate of 2, 4, 6 and 8 sccm is about 1, 5, 10 and >10 L. The Raman spectra indicate that the number of graphene layers increase with increasing the CH_4 gas flow rate, suggesting the graphene deposited using a lower CH_4 gas flow rate is of higher quality and possesses a lower degree of crystal defects. These results mean that the thickness of graphene prepared by RF-PECVD can be controlled by the ratio of CH_4 flow rate in a mixture of CH_4/Ar/H_2 gases.

Based on the above results, it follows that PECVD is a very powerful technique for the synthesis of large-scale graphene at relatively low temperature in a short time. In PECVD, plasma generated by electrical discharges is more effective at decomposing reactive gas than that in conventional CVD. With the assistance of plasma, reactive gas species (radicals) can be generated in high density at relatively low temperature [32–35]. Correspondingly, graphene can be prepared at low temperature in a short time. The process of graphene growth on the Ni film can be explained as follows: an extremely high concentration of reactive radicals is formed at lower temperature and pressure because of the assistance of plasma [34,35]. This means that the trace amount of CH_4 introduced into the PECVD chamber within a short time will produce a high concentration of carbon reactive radicals. During PECVD of graphene, the carbon atoms from decomposing CH_4 gas enter the interior of the Ni film. Upon cooling, the carbon atoms leave the interior of the Ni film, and segregate on its surface to form graphene because the solubility of carbon in Ni is temperature-dependent [15,17,18], as is schematically illustrated in Figure 5. In addition, an increase in the fraction of CH_4 in the mixture of gases also leads to an increased concentration of reactive carbon radicals [36]. Thus, the thickness of graphene can be controlled by either deposition time or CH_4 flow rate in the mixture of reaction gases.

3 Conclusions

We have demonstrated a low-temperature synthesis of high-quality, large-area single- or multilayer graphene on SiO_2/Si substrates covered with a Ni film using RF-PECVD. The number of graphene layers increases by increasing either deposition time or the ratio of CH_4 gas flow rate in the mixture of reaction gases. Single-layer graphene can be synthesized at a substrate temperature as low as 650°C with a gas flow rate ratio of 2/80/40 sccm (CH_4/Ar/H_2), and it can be easily transferred to other substrates by wet-etching Ni. These results show that RF-PECVD is a simple, low-cost, highly-effective and reproducible technique to synthesize graphene at relatively low temperature compared to conventional thermal CVD.

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