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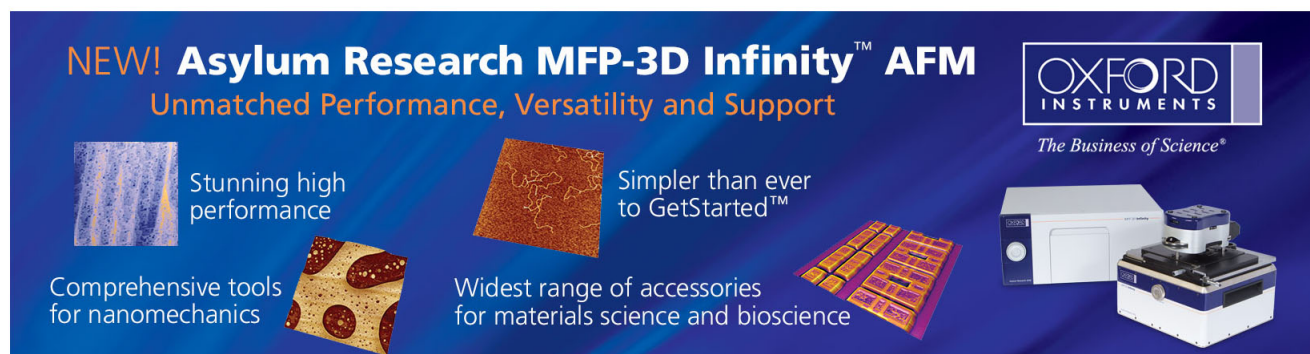Graphene growth by molecular beam epitaxy on the carbon-face of SiC
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Low-temperature grown graphene films by using molecular beam epitaxy

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Complete graphene film is prepared by depositing carbon atoms directly on Cu foils in a molecular beam epitaxy chamber at 300 °C. The Raman spectrum of the film has indicated that high-quality few-layer graphene is obtained. With back-gated transistor architecture, the characteristic current modulation of graphene transistors is observed. Following the similar growth procedure, graphitization is observed at room temperature, which is consistent with the molecular dynamics simulations of graphene growth. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768948]

Graphene, a material with unique characteristics, has attracted much attention in recent years.[1–8] To obtain this material, many different approaches have been developed such as exfoliation from highly ordered pyrolytic graphite (HOPG),[1–3] SiC sublimation,[4–6] and chemical vapor deposition (CVD).[7,8] For the exfoliation method, only flakes of graphene are obtained and for the SiC sublimation method, the high prices of the SiC substrates are the major concern for practical application. Therefore, the CVD technique has become a common approach to obtain graphene films. This method has exhibited advantages like large-area graphene growth and controllable layer numbers. In CVD method, Ni and Cu are two metals commonly used as the substrates. Different from the growth mechanisms of C atom dissolution and precipitation by using Ni templates, the low solubility of C atoms in Cu foil results in different graphene growth mechanisms of surface migration and self-align arranged construction on Cu foil.[9,10] Therefore, uniform single-layer graphene films can be obtained by using Cu substrate. The required graphene growth temperature by using CVD on Cu foil depends on the hydrocarbon source adopted to supply the C atoms. By using the common precursor methane, the growth temperature is usually around 1000 °C.[7,9] To decrease the growth temperature, different approaches have been investigated by using different precursors. By using hexane, ethanol, and alcohol, complete graphene films can be obtained at growth temperature ranged from 950 to 650 °C.[11,12] The lowest growth temperature reported in literature is 300 °C by using benzene in a low-pressure CVD chamber.[13] However, in that report, only graphene flakes instead of complete films are obtained. On the other hand, the growth temperature for Ni substrate is usually kept at 900–1000 °C due to the required C dissolve procedure.[8,14,15]

After growth, the graphene film transferring and reattachment procedure is required for both Ni and Cu substrates. In this case, it seems that the high-temperature growth procedure may not influence the following device fabrication. However, the graphene transferring procedure does not fit in the standard fabrication procedures for semi-conductor devices, which will limit the potential applications of this material. Therefore, direct growth of graphene at lower temperature would be the important first step to integrate graphene growth into semiconductor fabrication lines. By using the molecular beam epitaxy technique (MBE), the C atoms can be directly evaporated from the heated pyrolithic graphite (PG) filament and reach the substrate surfaces in atomic form. In this case, it seems to be no need for high substrate temperature during graphene growth, which makes the MBE technique a possible candidate for direct graphene growth at low growth temperatures. The other issue is the C concentration required for graphene growth. By using the effusion cell equipped in the MBE system, the carbon flux can be precisely controlled by adjusting the cell temperature. According to the work done by Loginova *et al.*, the graphene formation process begins with nucleation and then the graphene area expanding.[16] At the nucleation state, the carbon concentration needs to be few times higher than the concentration when expanding. However, with decreasing growth temperatures, the required C concentrations in both nucleation and expansion stages become less. Therefore, with the atomic carbon source and the reduced required carbon concentration, low-temperature growth may be the major advantage of MBE-prepared graphene.

In this paper, the graphene film is prepared by depositing carbon atoms directly on 100 μm Cu foils in a MBE chamber with 300 °C substrate temperature. The C atoms are supplied by an effusion cell with a heated PG filament. After growth, the graphene film formed on the Cu foil surface is transferred and reattached to a 600 nm SiO$_2$/Si substrate. The Raman spectrum of the film has shown significant G- and 2D-peaks and depressed D-peak, which suggest that high-quality few-layer graphene is obtained by using MBE at low substrate temperature 300 °C. The scanning tunneling microscope (STM) image of the film has also shown standard sp^2 bonding of C atoms. After fabricating the film into a back-gate transistor, the characteristic current modulation of graphene transistors is observed. Following similar growth procedure, the observed graphene flakes fully covered Cu foils with the substrate heater turned off suggest that graphitization can take place at near room temperature. We also

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carried out a series of molecular dynamics (MD) simulations of graphene growth and simulation results are in excellent agreement with the experimental observations. The results have exhibited the possibility of direct graphene growth at low temperature by using MBE.

Before growth, the 100 μm thick Cu foils are annealed in a furnace for crystallization. The furnace is filled with H_2/Ar mixture gas with fixed chamber pressure 7 Torr. The annealing temperature is 1000 °C and the annealing time is 10 min. The flow rate of H_2 and Ar are 150 and 500 sccm, respectively. The grained Cu foil is then transferred to a homemade MBE system to deposit C atoms by using Ribar carbon filament effusion cell. The cell temperature is set at 2173 °C, which corresponds to a carbon flux $\sim 5.3 \times 10^{11}$/cm^2 s and deposition rate of $\sim$0.2 nm/min. After 30 min of growth period, the sample is cooled to room temperature and then transferred out of the growth chamber. To transfer graphene from the Cu foil, a layer of polymethylmethacrylate (PMMA) is first spun on the sample and baked at 180 °C for 2 min. And then the Cu is removed with marble's reagent solution. After reattachment of the film to a p-type Si substrate with 600 nm SiO$_2$ on the surface, the PMMA is removed by using acetone. The STM image is taken by using a RHK-SPM 100 system under ambient circumstances. The Raman measurements are performed by using a HORIBA Jobin Yvon HR800UV spectrum system on the films transferred to SiO$_2$/Si substrates.

The 4.2 $\times$ 4.2 nm^2 STM image measured under tunneling current 1.05 nA and bias 1.6 V of the graphene film grown on a Cu foil at 300 °C is shown in Fig. 1(a). As shown in the figure, completely hexagonal structure of C atoms can be observed. These results suggest that by using the atomic C source, graphitization can take place at a low temperature of 300 °C. To verify if the graphene film is formed after high-temperature furnace annealing or MBE growth, the Raman spectrum of the Cu foil measured after high-temperature furnace annealing is shown in Fig. 1(b). No characteristic graphene Raman peaks are observed, which suggest that there is no graphene film formed after high-temperature furnace annealing. After transferring the graphene film from the Cu foil to a 600 nm SiO$_2$/p-type Si substrate, Raman measurements are performed on the film, which is shown in Fig. 1(c). Low D peak of the transferred film suggests that relatively few defects are observed on the film even with the low growth temperature of 300 °C. And from the ratio of 2D and G peak, it is estimated that 5–6 layers graphene is obtained, which is different from the self-limited process observed for CVD grown graphene on Cu foils.[14] Due to the low solubility of C atoms into Cu foils, the growth mechanisms of CVD-prepared graphene films on Cu foils are hydrocarbon gas decomposition and subsequent C atom adsorption to substrate surface. After the formation of the first layer of graphene film on Cu surfaces, C atom adsorption will not take place on the graphene surface, because such dehydrogenation reactions require Cu as surface catalytic material and, therefore, is self-limiting. For MBE-grown graphene, on the other hand, elemental carbon atoms are directly deposited onto the substrate via the Van der Waals interaction at low temperature (300 °C); hence, the layer number of the graphene films is determined by the
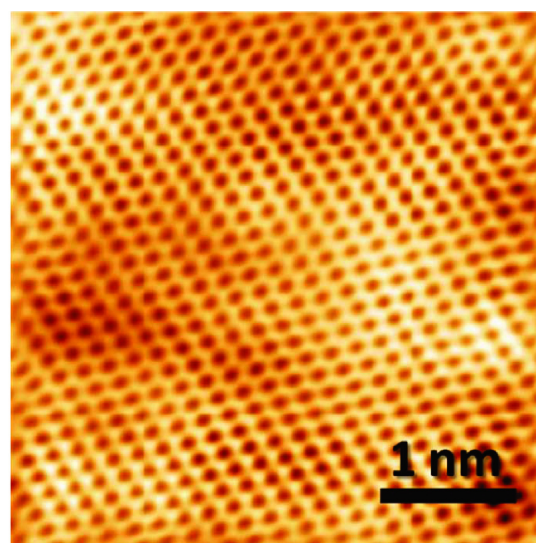
(a)

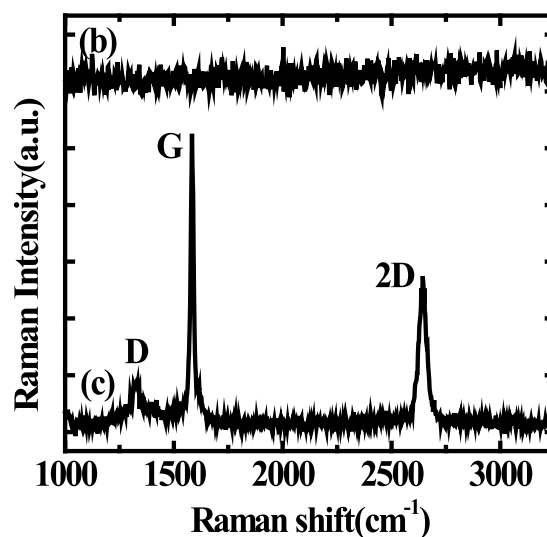FIG. 1. (a) The 4.2 $\times$ 4.2 nm^2 STM images of the graphene film grown at 300 °C measured under tunneling current 1.05 nA and bias 1.6 V showing complete hexagonal structure of C atoms and the Raman spectra of (b) the Cu substrate after high-temperature annealing and (c) the film transferred to a 600 nm SiO$_2$/p-type Si substrate.

amount of supplied C atoms. In this case, multilayer graphene film is observed by using MBE growth technique.

The graphene film transferred to the 600 nm SiO$_2$/p-type Si substrate is fabricated into back-gate transistors. The scanning electron microscope (SEM) image of the device is shown in Fig. 2(a). The graphene stripes are defined by using the standard photolithography procedure with O$_2$ plasma etching. After Au metal evaporation for source/drain terminals, a graphene transistor with 10 μm channel width and 50 μm channel length is fabricated. The drain currents of the device measured under different gate biases are shown in Fig. 2(b). As shown in the figure, significant current modulation is observed for the device. By fitting the curve using the equation $\mu = (dI_D/dV_g)/(\varepsilon V_D W/T_{ox}L)$, where T_{ox}, W, and L represent the gate dielectric thickness, channel width, and channel length, respectively, ε is the dielectric constant of dielectric layer, and V_D is the source-drain bias, the mobility 123.1 cm^2/(V·s) is obtained for this device.[17] The value is
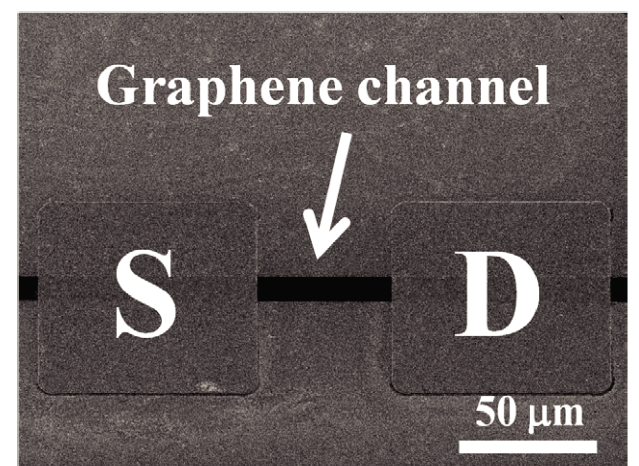
(a)
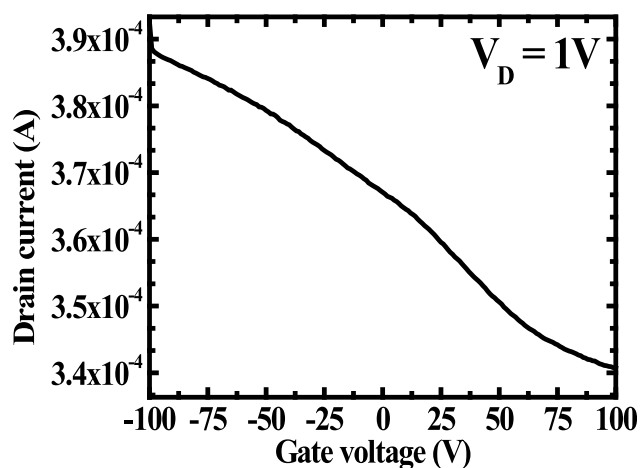
(b)

FIG. 2. (a) The SEM image of the graphene transistor and (b) the drain currents measured under different gate biases of the graphene back-gate transistor showing significant current modulation under drain voltage of 1 V.
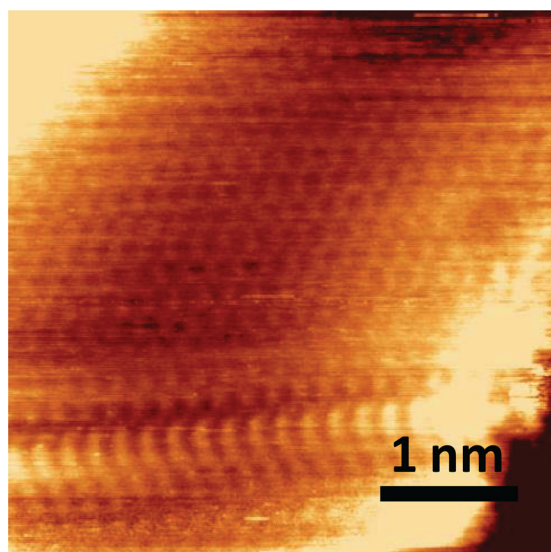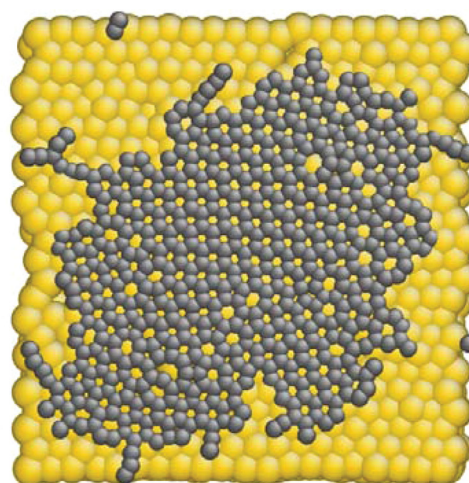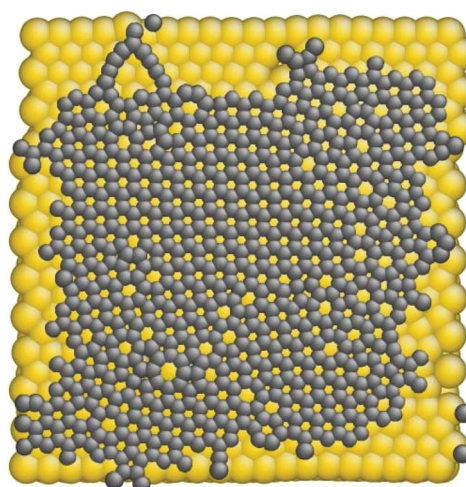

(a)

(b)

(c)

FIG. 4. Snapshots of MBE graphene growth from molecular dynamics simulation: (a) 573 K, 12 ns; (b) 573 K, 16 ns; (c) 300 K, 12 ns.

FIG. 3. The STM image of the graphene flake grown at room temperature.

compatible with CVD-prepared graphene films.[8] The results have demonstrated that by using MBE, the growth temperature of graphene films can be significantly reduced to 300 °C. The unique material characteristics of graphene can still be maintained at such a low temperature.

Although 300 °C is already a acceptable temperature for semiconductor fabrication lines, it would be interesting to see if graphitization would take place at even lower temperature, say, room temperature. Following the similar growth procedure, the same high-temperature annealed Cu foil is transferred into the MBE chamber for 30 min. C deposition with the substrate heater turned off. The STM measurement over the sample reveals that graphene flakes have covered the whole surface. The STM image over one of the flakes is shown in Fig. 3. Similar with the image shown in Fig. 1(a), hexagonal structure of C atoms is observed for the sample grown at room temperature. Compared with the film grown at 300 °C, the results suggest that although graphitization will take place at near room temperature, a little higher substrate temperature may still be required for C atom migration on the surface for more uniform and complete graphene film formation.

We also carried out MD simulations to simulate the MBE growth processes of graphene on Cu substrate at two temperatures: 300 °C (i.e., 573 K) and room temperature (i.e., 300 K). In our MD simulation, one carbon adatom was deposited onto Cu (111) surface every 2 ps. The initial temperature of carbon adatoms was set to 2000 K and these carbon adatoms will gradually dissipate their thermal energies on Cu surface. We used the AIREBO potential[18] to describe the interaction between carbon atoms and LAMMPS MD simulation package to perform MD simulations. During our deposition simulations, some carbon adatoms desorb and we remove these carbon atoms from our system. Figure 4 displays the snapshot of MBE-grown graphene films at 573 K (Figs. 4(a) and 4(b)) and at 300 K (Fig. 4(c)). From Fig. 4, we can clearly see the formation of graphene film on Cu surface. Comparing Figs. 4(a) and 4(c), we can find that more carbon adatoms desorb in the 573 K simulation because the graphene film grown under 573 K has less graphene coverage comparing with that grown under 300 K. Close examinations of the films with similar surface coverage (i.e., Figs. 4(b) and 4(c)) indicate that graphene film grown at higher temperature (i.e., 573 K) has less defects comparing with that grown at room temperature. Therefore, the MD simulations performed in the present study confirms the possibility of graphene growth at low temperature.

In conclusion, with the experimental results and the theoretical simulations discussed in this paper, graphene growth by using MBE can be a promising technique for low-temperature graphene formation, which is advantageous for the integration of graphene growth into standard semiconductor fabrication lines. The growth mechanism of this approach may also be utilized for direct graphene growth on semiconductor substrates with the assistance of very thin Cu films deposited prior growth. Further investigations are still necessary for the development of this application.

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