Few-layer graphene film fabricated by femtosecond pulse laser deposition without catalytic layers

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The films of few-layer graphene are formed through laser exfoliation of a highly ordered pyrolytic graphite (HOPG), without a catalytic layer for the growth process. The femtosecond (fs) laser exfoliation process is investigated at different laser fluences and substrate temperature. For fs laser exfoliation of HOPG, the few-layer graphene is obtained at 473 K under an optimal laser fluence. The formation of few-layer graphene is explained by removal of intact graphite sheets occurred by an optimal laser fluence ablation. The new insights may facilitate the controllable synthesis of large area few-layer graphene.

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Since the discovery of two-dimensional (2D) graphene in 2004[1], gaining a huge amount of research interest in recent years due to its exceptional optical, electrical, chemical, and mechanical properties. For example, grapheme-based photodetectors have been fabricated for high-speed optical communication, wide band optical detection, terahertz detection and other applications[2–7]. To take advantage of graphene's saturable absorption, the graphene is applied to the Q-switching and mode locking technology[8,9]. There are various methods of graphene preparation including: mechanical exfoliation, chemical vapor deposition (CVD), Epitaxial growth on SiC, oxidation-reduction method, and pulse laser deposition (PLD) technology[1,10–16]. Among these methods, the PLD is relatively simple and fast established vacuum technology for graphene film growth and has been a popular method for fabricating graphene by a long-pulsed laser[14–16]. For instance, freestanding 2D few-layer graphene was formed through laser exfoliation of highly ordered pyrolytic graphite (HOPG)[14,15], which avoiding the high temperature and metal catalyst in epitaxial growth. However, the size of obtained graphene films is too small that cannot provide base for integrated device fabrication. Furthermore, the femtosecond (fs) pulse laser is applied rarely for the few-layer graphene of pulsed laser deposition. To address this issue, and to explore the mechanism of the formation of graphene deposited by fs pulse laser exfoliation of HOPG, a simple and fast fs pulse laser exfoliation of HOPG is demonstrated.

In this Letter, the formation of few-layer graphene is achieved through fs pulse laser exfoliation of HOPG without a catalytic layer. The laser exfoliation process is investigated as a function of laser fluence and different substrate temperature. Our findings suggest that the few-layer graphene can be obtained at an optimal fluence (0.3 J/cm^2). A scanning electron microscope (SEM), an atom force microscope (AFM) and a Raman spectroscopy are sued to study the few-layer graphene film.

The experimental setup is shown in Fig. 1. After loaded with a commercial HOPG as the target and a bare n-doped silicon (Si) (1 0 0) wafer as the substrate, and the distance between the HOPG target and the silicon substrate is 50 mm, the chamber is vacuumed to 10^{-6} Torr. In the experiment, the irradiation source with laser fluences from 0.1 to 0.5 J/cm^2 is an amplified Ti:sapphire fs laser system, which provides 80 fs pulses of an energy of 3 mJ/pulse operated at a 1 kHz repetition rate at a central wavelength of 800 nm. The beam power profile is Gaussian. After passing through attenuator, the fs laser pulses is focused through a 400 mm lens toward HOPG at an angle of 45°. In the experiment, the irradiation time is controlled by an electromechanical shutter, and the same spot of the HOPG is irradiated for 4 pulse. The substrates are mounted on a continuously rotating target in order to guarantee a homogeneous consumption, during

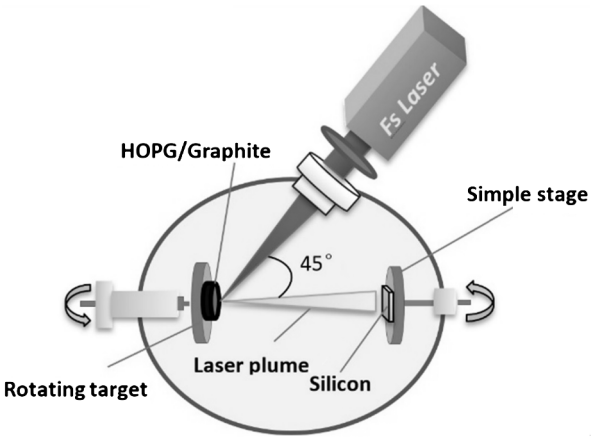

Fig. 1. Schematic image of the laser deposition system.

the ablation process. PLD is carried out at two different substrate temperature (300 and 473 K) and three laser fluences (0.1, 0.3, and 0.5 J/cm^2). A SEM, an AFM, Raman spectrometer excitation wavelength of 514 nm were used to study the simples.

Figure 2 shows the Raman spectra of graphene films deposited at 473 K using three different laser fluences (0.1, 0.3, and 0.5 J/cm^2). Visible Raman spectroscopy is a suitable technique to probe the structure of sp^2 rich carbon as visible excitation is highly sensitive toward sp^2 bonding and its photons resonate with the π states. The spectra of graphene consist of three peaks at 1350, 1590, and 2700 cm^{-1}, G band around 1590 cm^{-1} and 2D band near 2700 cm^{-1} are the most prominent Raman features of graphene[17]. The weak D band near 1350 cm^{-1} refers to the disorder in sp^2 carbon network[18]. The G peak is characteristic of the carbon sp^2 structure and a nonresonant scattering process, reflecting its asymmetric and cleanliness. It occurs due to the in-plane vibrations of the sp^2 carbon whether in chain or ring form. The peak at near 2700 cm^{-1} is the second order D peak, which is generally referred to as the 2D peak, is present even in the absence of defect. No 2D peak was detected for sample at two fluence of 0.1 and 0.5 J/cm^2, and the deposited carbon material are amorphous on Si surface. The 2D peak is only seen at a laser fluence of 0.3 J/cm^2, as shown in Fig. 2. The ratio of intensity of G band to 2D (I_G/I_{2D}) is often used to extract the number of layers of graphene[17,19]. The I_G/I_{2D} ratio is 0.5 for monolayer graphene and increases with increase in number of layers, since the G band becomes more prominent[20]. By this approximation, the I_G/I_{2D} ratio about 1.07 at the laser fluence of 0.3 J/cm^2, which transformed the three into four layers, clearly showing features of few-layer graphene. The full width at half-maximum (FWHM) of the 2D band for the film deposited at 0.3 J/cm^2 is 80 cm^{-1}, which is higher than 65 cm^{-1}, reported for graphene[21]. Figure 3 shows an AFM and three-dimensional (3D) image indicating a 3.49 nm thick film. Figure 4 shows optical image of a PLD-grown few-layer graphene film (blue) deposited at 473 K with a laser fluence of 0.3 J/cm^2. The few-layer graphene film transferred to a polymentyl–methacrykate (PMMA)/Si substrate (gray background) is visible on 1 μm (PMMA) using white light. The single layer usually appear as a light blue sheet, and the color becomes darker as the number of layers

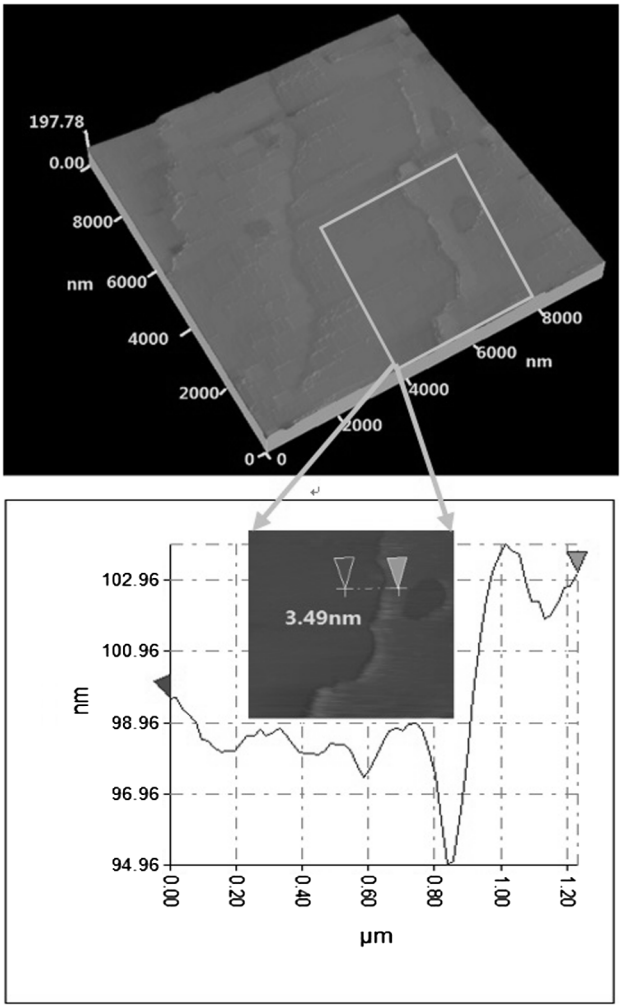

Fig. 3. AFM and 3D image indicating a 3.49 nm thick film deposited at 473 K with a fluence of 0.3 J/cm^2.

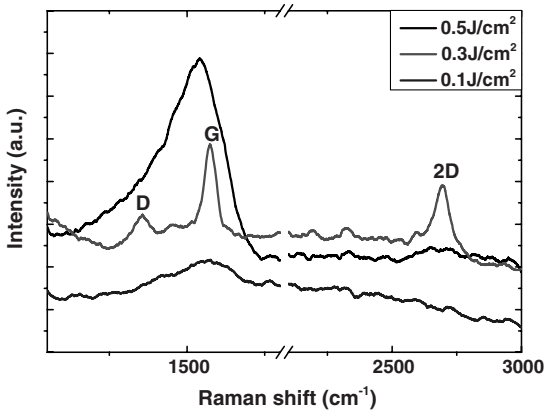

Fig. 2. Raman spectra of samples deposited at 473 K by three different pulsed laser fluences exfoliate the HOPG.

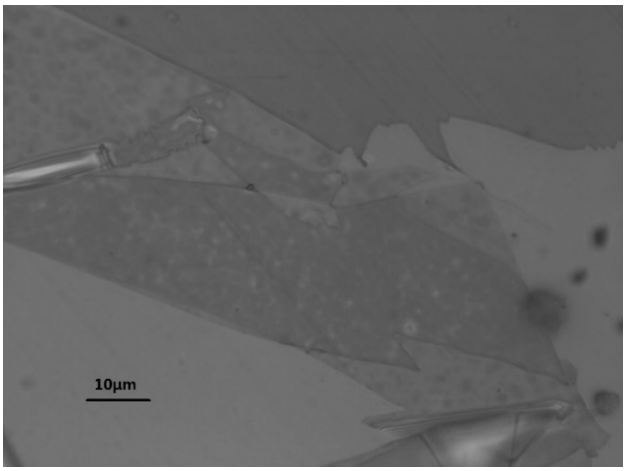

Fig. 4. Optical image of a PLD-grown few-layer graphene film (blue) transferred to a PMMA/Si substrate (gray background).

increases[22]. In our experiment, a darker blue film is found, as shown Fig. 4. Meanwhile, the blue of the few-layer graphene is darker than the optical image of a CVD-grown graphene film transferred to a SiO_2/Si substrate[11].When white light though the substrate and reflect to the surface of the film[23], we suggest that a thicker substrate lead to weaken the intensity of white light, resulting in darker the film[4].

Figure 5 shows that the Raman spectra of samples deposited at 300 K by three different pulsed laser fluences (0.1, 0.3, and 0.5 J/cm^2). We find that the 2D is also only obtained at 0.3 J/cm^2, as shown in Fig. 5. Meanwhile, the 2D (2715 cm^{-1}) and G peak of the sample deposited at a fluence of 0.3 J/cm^2 are broad largely, and G peak deviates the G (1590 cm^{-1}) peak of pristine graphene, as shown in Fig. 5. For fs pulse laser irradiating the solid target, the high energy particles are ejected and the particles have high temperature. So, when the plume interacts with substrate, the carbon particles react to the around oxygen, and the sample thus is oxidized. Furthermore, the frequency of thermal vibrations of atoms is inertial at the low temperature with the substrate. According to the results of two experiments, only an optimal fluence of laser can few-layer graphene be deposited by fs pulse laser exfoliation of HOPG, and the high substrate temperature promotes the layered growth and is beneficial for the graphene growth.

According to the previous study about the physical mechanisms for damage formation in graphite films[24], the low fluence ablation threshold (>2.0 eV/atom) is the removal of intact graphite sheets and does not involve melting. In contrast, the high fluence threshold (>3.3 eV/atom) corresponds to bond breaking processes inside the graphite layers and leads to ultrafast melting and expansion of the film. According to Refs. [24,25], in this experiment, the intensity was determined so that the graphite films absorb $E_0 = 0.9, 2.7,$ and 4.5 eV, respectively, corresponding a carrier density of $n_c = 6.1 \times 10^{22}$ cm^{-3}, $\lambda = 800$ nm and three fluences of $F \approx 0.1$, 0.3, and 0.5 J/cm^2, respectively[25,26]. The ablation threshold of HOPG is about 0.23 ± 0.05 J/cm^2 for the ultrashort laser pulse(s) of the wavelength $\lambda = 800$ nm. The laser fluences of 0.3 J/cm^2 is more close to threshold of 0.23 ± 0.05 eV/atom. Meanwhile, the optimal pulse laser fluence (0.3 J/cm^2) leads to enough strong vibrational excitation of the graphite layers, resulting in a significant movement of the atoms perpendicular to the graphite planes. Therefore, few-layer graphene is obtained at 0.3 J/cm^2. For the high laser fluence of 0.5 J/cm^2, the energy density is enough to break the C-C bond, and thus few-layer graphene is not obtained. In addition, Russo *et al.* performed a simple, green, and scalable method for the production of porous graphene[26]. It is found that the formation of porous graphene depends on the fs laser ablation energy. It is further demonstrated that fs laser ablation energy plays an important role in the formation of the graphene.

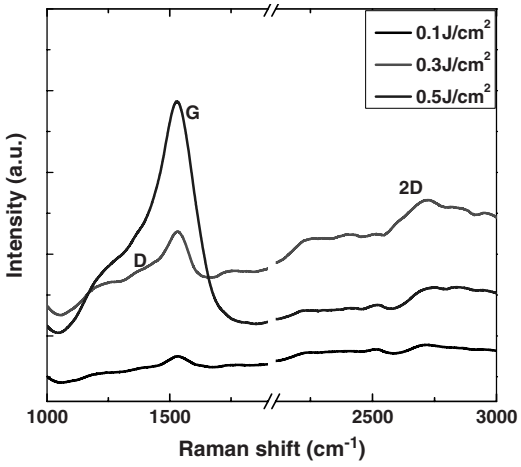

Fig. 5. Raman spectra of samples deposited at 300 K with different pulsed laser fluencies.

In conclusion, few-layer graphene film is fabricated on Si substrates using the fs laser exfoliation of HOPG. The fs laser exfoliation process is investigated at different laser fluence and substrate temperature. The formation of few-layer graphene films deposited at 473 K is only obtained at an optimal fluence. The formation of few-layer graphene is explained by a removal of intact graphite sheets occurred by an optimal laser fluence ablation. These results are valuable for understanding the growth mechanism of graphene, and the new insights can facilitate the controllable synthesis of large area few-layer graphene.

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