High-quality, single-layered epitaxial graphene fabricated on 6H-SiC (0001) by flash annealing in Pb atmosphere and mechanism

T W Hu 1,2, X T Liu 2, F Ma 1,2, D Y Ma 2, K W Xu 2,3 and P K Chu 1

1 Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People’s Republic of China
2 State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, Shaanxi, People’s Republic of China
3 Department of Physics and Opt-electronic Engineering, Xi’an University of Arts and Science, Xi’an 710065, Shaanxi, People’s Republic of China

E-mail: mafei@mail.xjtu.edu.cn, kwxu@mail.xjtu.edu.cn and paul.chu@cityu.edu.hk

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Abstract
High-quality epitaxial graphene is produced on silicon carbide by flash annealing of 6H-SiC in a lead (Pb) atmosphere at ~1400 °C for 30 s. Nearly three top bilayers of SiC are decomposed due to fast heating and cooling, and sublimation of Si atoms from SiC is retarded by the Pb atmosphere. The synergetic effects promote the growth of continuous single-layered graphene sheets on the SiC terraces, and a model is established to elucidate the effects and growth mechanism.

Keywords: flash annealing, epitaxial graphene, Pb atmosphere

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene has been widely studied since its discovery due to its unique properties [1, 2] and potential application to optoelectronics, solar cells, and liquid crystal displays [3, 4]. Several techniques have been developed to fabricate graphene. However, mechanical exfoliation used to prepare graphene sheets typically has low production efficiency [5], and although oxidation and reduction of graphite can be used to fabricate large-scale graphene sheets, unwanted defects are common [6]. Chemical vapor deposition is used to prepare large-scale high-quality graphene sheets on metals such as Cu [7, 8] and Ni [9, 10], but industrial large-scale production by this technique is still challenging. Hence, researchers continue to explore new methods to fabricate high-quality graphene directly on insulators, and thermal decomposition of silicon carbide (SiC) has attracted increasing attention [11]. Lin et al fabricated epitaxial graphene on a 50 mm SiC wafer by annealing at 1450 °C and produced field-effect transistors with a cutoff frequency as high as 100 GHz [3]. This has led to further investigation of the mechanism of thermal decomposition of SiC as well as potential applications [11, 12].

At a high temperature, Si—C bonds break, and Si atoms sublime from the SiC substrate, while the remaining carbon atoms nucleate and grow epitaxially [12–14]. Since thermal decomposition of SiC in an ultra-high vacuum is not a self-limiting process, the epitaxial graphene tends to have a rough surface, and discontinuity and pits are common [15, 16]. In order to improve the graphene quality, Konstantin et al conducted thermal decomposition in an argon (Ar) atmosphere to confine sublimation of Si atoms and to provide enough time for the carbon atoms to diffuse so as to promote the growth of large graphene domains [17]. de Heer et al have further developed this confinement controlled sublimation process [18]. Although continuous graphene can be prepared, it is still difficult to control the thickness because of the long annealing time. Hence, it is crucial to considerably reduce the annealing time to improve the formation of single-layer graphene sheets.
In the work reported in this letter, flash annealing is performed in a lead (Pb) atmosphere to fabricate continuous and single-layered graphene on SiC. In addition to retarding Si sublimation by the Pb atmosphere, the metal atoms near the disordered C atoms weaken the C—C bonds to promote graphitization [19], a process resembling metal-induced crystallization of amorphous Si at low temperature annealing [20]. The synergetic effects rendered by flash annealing and the Pb atmosphere are investigated systematically by in situ scanning tunneling microscopy (STM), which might be extended to other metals. Atomic force microscopy (AFM), Raman scattering, and x-ray photoelectron spectroscopy (XPS) are adopted to characterize the microstructure, and a model is proposed to elucidate the underlying mechanism.

2. Experiment

The experiments were performed on a commercial USM-1400 system (Unisoku) comprising an ultra-high vacuum molecular beam epitaxy chamber and an in situ low-temperature STM apparatus. Si- and C-terminated 6H-SiC (0001) wafers purchased from Tanke Blue Semiconductor Co. Ltd were degassed at ∼550 °C for at least 8 h by direct-current heating to obtain a clean surface. Pre-treatment and flash annealing were conducted in the MBE chamber at a base pressure of 10^{-10} Torr. Surface reconstruction in the SiC unit cells occurred at a high temperature [13] that was controlled by the application of a direct current of 1.8 ∼ 2.2 A and measured by an optical pyrometer. The (6√3 × 6√3)R30° buffer layer emerged on the SiC surface after heating at ∼1200 °C for 10 min [21]. Afterwards, four annealing processes are involved and compared with each other: (1) flash annealing at ∼1400 °C in the Pb atmosphere for 30 s, (2) flash annealing at ∼1400 °C in an atmosphere without Pb for 30 s, (3) flash annealing at ∼1700 °C in an atmosphere without Pb for 5 s, and (4) annealing at ∼1400 °C for 5 min. The Pb atmosphere is produced by pre-deposited Pb islands on a buffer layer or under a Pb flux at a rate of ∼1 monolayer per minute (ML/
Two or three annealing cycles were employed to produce graphene sheets over the SiC terrace. Based on this, we would like to discuss the effects of flash annealing and the Pb atmosphere on the quality of e.g. sheets. In situ STM images were acquired in the constant current mode at 77 K, and electrochemically etched W tips were used. Image processing was performed using WsXM [22]. AFM was adopted to characterize the samples with rough surface morphologies. Raman spectra were measured in the Nanofinder 30 system (Tokyo Instruments, Inc.). A laser with a wavelength of 533 nm and a power of 1 ∼ 5 mW was used, and the size of laser spot was about 1 ∼ 1.5 μm. XPS (Physical Electronics PHI 5802) was conducted with a monochromatic Al Kα source at 350 W. The electronic conductivity was measured by a four-point probe method in a commercial semiconductor characterization system (Keithley 4200).

3. Results and discussion

Figure 1(a) displays the morphology of the $6\sqrt{3}$ buffer layer, which generally appears in the embryonic stage before graphitization of residual carbon atoms during thermal decomposition of SiC. The $6\sqrt{3}$ precursor affects the quality of e.g. sheets greatly [12, 23]. The original SiC steps can still be identified from the $6\sqrt{3}$ surface, as indicated by the white dashed lines. As denoted by the blue arrows, pits with different sizes are densely distributed on the terraces and may act as the passages for Si atoms underneath to escape from the SiC substrate [24–26]. If there are no extraneous atoms for equilibration in the sublimation process, more and larger pits will be produced, and, consequently, the decomposed SiC surface is rough [16]. In our experiments, Pb instead of Si and Ar is used to maintain the balance. Figure 1(b) shows the Pb islands with a coverage of about three to four monolayers on
the $6\sqrt{3}$ surface. During the flash annealing process, Pb atoms in the islands evaporate and can produce a metal atmosphere in order to lower the evaporation rate of Si atoms from SiC substrates—the same effect as in the gas atmosphere. Figure 1(c) depicts the STM image of the sample in figure 1(b) after flashing annealing at ~1400 °C. Regular terraces covered by uniform graphene are clearly shown, and the surface is indeed a mixture of single-layer (S) and bilayer (B) e.g., but the single-layer graphene is dominant, exhibiting the surface is indeed a mixture of single-layer (S) and bilayer (B) e.g., but the single-layer graphene is dominant, exhibiting the surface topography of the graphene. For the same reason, other metals such as silver (Ag) and indium (In) can also be used to promote the growth of e.g. This work is continued in our group.

The pre-deposited Pb islands on the buffer layer evaporate during flash annealing. Hence, the Pb atmosphere, rather than solid Pb islands, constitutes the necessary condition for the formation of high-quality e.g. Therefore, the fabrication process can be simplified. That is, the SiC substrate undergoes flashing in a Pb flux of ~1 ML min$^{-1}$ at ~1400 °C. The STM image in figure 2(a) reveals a uniform morphology on the SiC terraces corroborated by the ordered height profile across the terraces shown in the bottom panel. The results resemble those in figure 1(c). Figure 2(b) shows the AFM image of the epitaxial graphene flashed at ~1700 °C without the Pb atmosphere, in which graphene sheets become fragmented. The surface becomes quite rough due to the melting of the SiC surface, but the atomic-resolution STM image cannot be observed, although the Raman spectrum characteristic of single-layer graphene is obtained. Raman scattering conveys useful information about the defects (D band) and in-plane vibration of sp$^2$ carbon atoms (G band), as well as the stacking order (2D band) of graphene, and can be used to determine the layer number [30]. If the 2D band has a sharp symmetrical peak with an intensity larger than that of the G band, the graphene sheet has a single-layered structure [31]. The raman spectrum in figure 2(c) is obtained with an accumulation time of 20 s. The intensity ratio of the 2D and G peaks, I$_{2D}$/I$_G$, is 1.96, and the full-width at half-maximum (FWHM) of the 2D peak, W(2D), is 50.8 cm$^{-1}$. Therefore, the Raman results suggest that the fabricated graphene is only one atomic layer thick, or at least nearly single-layer on the mostly SiC surface. Figure 2(d) presents the 10 × 10 um Raman map of the 2D peak across the surface, shown in figure 2(b). The intensity fluctuation is not appreciable, indicating that the graphene is relatively uniform in thickness. In fact, the Raman spectrum is an average over the laser beam size on the order of a micron. Combined with the Raman spectrum of figure 2(c), the Raman map of figure 2(d) just shows that the SiC surface is almost completely covered by single-layer graphene. But it cannot exclude the existence of small bilayer domains, according to the uniformity of the Raman signal.

Figure 3 depicts the C 1s and Si 2p XPS spectra. As shown in figure 3(a), the peaks at binding energies of 283.5 eV and 286.3 eV of C 1s stem from the SiC substrate [32, 33]. The peak at 284.5 ± 0.1 eV (sp$^2$) is attributed to graphene (G) on SiC [17] and that at 284.9 ± 0.1 eV corresponds to the C-rich amorphous buffer layer (α-C) underneath the graphene [13, 25]. Figure 3(b) shows two peaks at

![Figure 3. XPS spectra: (a) C 1s and (b) Si 2p. The red and cyan contour lines are measured from the samples flashed at ~1400 °C in the Pb atmosphere and at ~1700 °C without Pb, respectively. The wide asymmetrical peaks are deconvoluted into several Gaussian components.](image-url)
101.1 eV and 101.7 eV for Si 2p, corresponding to Si–C bonds in the SiC substrate [33], and that at 102.3 eV arises from Si–Si bonds. Compared to the sample flashed at ~1400 °C in the Pb atmosphere, the C 1 s peak at 283.5 eV disappears, and the Si 2p peak shifts to 102.3 eV, flashed at ~1700 °C without Pb. It may be due to accumulation of Si clusters between the graphene and the buffer layer. The Si clusters may produce a ridge-like morphology on the rough graphene surface [14, 34], and, as a result, the XPS signal from the SiC substrate may not be detected from the rough surface. As illustrated above, the Pb atmosphere evaporated from the buffer layer or from the flux source, the same as the Ar and Si atmosphere, can produce an extra pressure to lower the evaporation rate of Si atoms from SiC substrates. In such a case, there is enough time for C atoms to diffuse on the buffer layer surface and grow into large-domain graphene. Flash annealing is done through a very fast heating and cooling treatment that is similar to the rapid thermal annealing process. Thus, the reaction between Pb atoms and the graphene or SiC substrate does not take place, and Pb atoms will be removed during flash annealing. So no Pb signal could be tested by XPS.

A model is proposed to elucidate the mechanism. Figure 4(a) schematically shows the original SiC substrate with a buffer layer on the terraces. During flash annealing, nearly the three top bilayers of the SiC terraces are decomposed due to fast heating and cooling, producing single-layered graphene on the buffer layer. The Pb atmosphere retards evaporation of Si atoms, further promoting the growth of graphene in the step-flow mode. This process is schematically displayed in figure 4(b) and confirmed by figures 1(c) and 2(a). In contrast, during flash annealing at ~1700 °C without Pb, thermal decomposition and evaporation of Si atoms increase, and more bilayers on the SiC terraces are decomposed in spite of the short time. Moreover, the SiC surface is partly melted. This produces irregular clusters (yellow cycles) between the graphene and the SiC substrate as well as a rough surface topography, as schematically illustrated in figure 4(c) and observed from figure 2(b).

Figure 5 shows the measured electronic conductivity. Apparently, the conductivity of graphene on SiC is two orders of magnitude higher than the SiC surface. To some degree, it indicates the formation of high-quality graphene sheets on SiC. In addition, Raman scattering provides more information about the quality of the materials, and multiple spectra are acquired from different regions of each sample to improve the statistics. All the Raman spectra in figure 6 are obtained at the accumulation time of 2 s. This leads to the lower signal-to-noise ratio. But if the Raman spectra are fitted by Origin software, the figure quality can be considerably improved.
and it is sufficient to roughly evaluate the fabrication process of graphene by comparing the FWHM of the 2D peak and the intensity ratio of 2D and G peaks from the fitted Raman spectra [35, 36].

Figure 6(a) presents the Raman spectrum of the graphene sheets prepared by mechanical exfoliation and transferred onto a Si substrate with a silicon dioxide layer. The D, G, and 2D peaks of the exfoliated graphene are observed at 1326.5 cm\(^{-1}\), 1587.0 cm\(^{-1}\), and 2649.1 cm\(^{-1}\), respectively. The D peak indicates the existence of defects in graphene such as grain boundaries, edges, vacancies, and so on [37]. The FWHM of the 2D peak is 36.1 cm\(^{-1}\), and the intensity ratio of the 2D and G peaks (I\(_{2D}/I_G\)) is 3.62, which is characteristic of single-layer graphene [30, 38]. Figure 6(b) exhibits the Raman spectrum of the sample flashed at \(\sim 1400^\circ\)C in the Pb atmosphere. The D peak is obscure, I\(_{2D}/I_G\) is 1.32, and the FWHM of the 2D peak is 40.5 cm\(^{-1}\)—that is, close to that of the exfoliated graphene in figure 6(a). The results indicate that large-scale, single-layered graphene sheets with a small density of defects are fabricated (also confirmed by the STM images). Compared to the 2D peak of the exfoliated graphene (figure 6(a)), a shift from 2649.1 cm\(^{-1}\) to 2682.1 cm\(^{-1}\) of about 33 cm\(^{-1}\) is observed from the flashed sample (figure 6(b)) as a result of thermal compressive stress [39]. The stress can be evaluated according to the relationship, \(\sigma = \lambda \alpha\), in which \(\sigma\) stands for the stress in graphene, \(\lambda\) is the relative shift of the 2D peak with respect to that at zero strain, and \(\alpha\) is the constant of stress coefficient with an empirical value of 7.47 cm\(^{-1}\) GPa\(^{-1}\) [30, 35]. Accordingly, the compressive stress is about 4.4 GPa in the epitaxial graphene. Given that the elastic modulus of graphene is in the range of 900–1100 GPa [40], the strain is in the range of 0.40–0.49%. It will affect the band structure as well as the electronic and optical properties of the graphene on SiC [41]. Figure 6(c) shows the Raman spectrum of the sample flashed at \(\sim 1400^\circ\)C but without the Pb atmosphere. The larger FWHM (62.3 cm\(^{-1}\)) of the 2D peak indicates the formation of more-than-one-layer graphene sheets [35, 36]. The results are similar to the reported results [27]. Figure 6(d) shows the Raman spectrum of graphene prepared by thermal annealing at \(\sim 1400^\circ\)C for 5 min. I\(_{2D}/I_G\) is 0.45 (<1), and a slightly asymmetrical 2D peak with a large FWHM of 75.2 cm\(^{-1}\) is identified at 2688.0 cm\(^{-1}\), indicating that the graphene has a multi-layered structure [35, 36]. Therefore, flash annealing for a short time is crucial to fabricate single-layer graphene, and the Pb atmosphere is beneficial to improve the formation of uniform and ordered graphene.

4. Conclusions

In summary, a simple and effective approach to fabricate large-scale and high-quality graphene by flash annealing in a Pb atmosphere is described. Nearly the top three bilayers on the SiC substrate are decomposed due to the fast heating and cooling process, and evaporation of Si atoms from the SiC surface is retarded significantly by the Pb atmosphere, resulting in confined sublimation. A model is postulated to explain the growth process and underlying mechanism. This technique is potentially useful for graphene-based electronic devices.
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