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We describe a process for the growth of a single, electronically decoupled graphene layer on SiC(0001). The method involves annealing in disilane to (1) prepare flat, clean substrates, (2) grow a single graphene layer, and (3) electronically decouple the graphene from the substrate. This approach uses a single process gas, at μTorr pressures, with modest substrate temperatures, thus affecting a drastic simplification over other processes described in the literature. © 2014 AIP Publishing LLC.

Graphene growth at SiC surfaces has been extensively studied,1-4 and the basic mechanisms of growth are now well understood. At temperatures above 1100°C, the SiC surface decomposes in vacuum. The liberated Si evaporates while the remaining carbon atoms coalesce to form graphene.1 Controlling the decomposition process in ultra high vacuum is difficult because the mobility of carbon atoms at the surface is relatively low at the temperatures at which SiC begins to decompose. Poor carbon mobility leads to small domain size, non-uniform layer thickness, and pit formation.5 One way to circumvent the low mobility is to raise the decomposition temperature. This can be done by performing the decomposition in atmospheric pressures of an inert gas, e.g., argon.4 The argon causes a fraction of the evaporating Si atoms to be reflected back towards the surface, effectively raising the decomposition temperature. However, this method requires relatively high gas pressures, making in situ monitoring difficult. Tromp and Hannon showed6 that a silicon-containing background gas has a similar effect. That is, SiC decomposition will not occur if the background Si pressure exceeds the vapor pressure of Si over SiC. An advantage of this approach is that the required gas pressures are modest—in the 10^-6 Torr range—allowing in situ imaging9 and monitoring7 of the graphene growth.

The first graphene layer that forms interacts strongly with substrate. In fact, this “buffer layer” is insulating and does not exhibit the characteristic band structure or high carrier mobility of graphene.8,9 However, the morphology of the buffer layer is often superior to that of thicker graphene films. Furthermore, due to the nature of the decomposition process, a uniform buffer layer can be easier to produce than a uniform monolayer (1 ML) film (i.e., a “monolayer” films consists of the buffer layer plus one additional graphene layer). These factors have spurred the search for methods to electronically decouple the buffer layer from the substrate. For example, it has been shown that the intercalation of H,10 O,11 Li,12 and Si13 will effectively decouple the graphene from the substrate. Here, we show that the buffer layer can be decoupled by annealing in modest pressures of disilane, which leads to the formation of a 1 × 1 phase, followed by a self-limiting 3 × 3 phase. Both phases electronically decouple the buffer layer from the substrate. Combining growth of the buffer layer and decoupling of the buffer layer in a single growth run results in a single process for producing decoupled monolayer graphene films on SiC(0001).

Annealing in disilane can be used to (1) clean the SiC surface,2,14 (2) raise the SiC decomposition temperature,6 (3) control the growth rate and morphology of the buffer layer,6 and (4) electronically decouple the buffer layer from the substrate.

Graphene synthesis was done in a low-energy electron microscope15,16 equipped with an in-line energy filter for spatially resolved electron spectroscopy.17 Clean, well-ordered SiC(0001)-6H surfaces were prepared by first annealing for several minutes in 10^-6 Torr disilane at 800°C to remove residual oxygen, replacing the conventional high-pressure (milibar), high-temperature (1800°C) annealing in H2 gas. The temperature was then increased to 1100°C while surface step structure was imaged using LEEM. At this temperature, steps are mobile and imperfections in the surface morphology can be annealed out without forming graphene. Annealing continued until a uniform array of straight steps developed. In the previous work,14 we showed that this procedure results in the formation uniform surfaces with 0.75 nm high steps (i.e., three SiC bilayers), avoiding the formation of extended facets often observed after high temperature H etching. The graphene buffer layer was then grown by raising the temperature to approximately 1300°C while imaging the surface with LEEM. Growth was terminated by quickly reducing the sample temperature to below 500°C. Control of the graphene growth rate allowed us to prepare two types of surfaces: in the first, graphene growth was terminated when the surface coverage was approximately 75%, leaving 25% of the surface as clean SiC. In the second case, a complete graphene buffer layer was formed.

We first describe the results from surfaces with an incomplete buffer layer. As shown in Fig. 1(a), the graphene-covered areas of the surface exhibit the expected 6√3 × 6√3 low-energy electron diffraction (LEED) pattern characteristic of the graphene buffer layer strongly coupled to the SiC(0001) substrate. Si intercalation was accomplished by annealing the surface at 700°C in a background pressure of disilane, which was increased to a final value of 1.2 × 10^-6 Torr over a period of 600 s. After about 300 s of exposure, nucleation of a 1 × 1 phase is observed (marked “B” in Fig. 2). The nucleation takes place at the edges of the graphene domains, i.e., at the boundaries between the buffer layer and the clean SiC surface. The microspot low-energy electron diffraction (μLEED) pattern, recorded using a 2 μm
diameter illumination aperture, is shown in Fig. 1(b). The pattern corresponds to the superposition of diffraction from graphene and a $1 \times 1$ SiC(0001) structure. A similar diffraction pattern is observed when oxygen is intercalated between the buffer layer and SiC surface. $^{11}$ A $1 \times 1$ phase was also observed by Xia et al., who annealed a two layer film (buffer layer and one additional graphene layer) after deposition of Si at room temperature. $^{12}$ The silicon film in that work was deposited using molecular beam epitaxy, whereas our process uses a disilane background pressure. With continued exposure to disilane, all of the graphene areas adopt the $1 \times 1$ structure ($t = 1470$ s). Following completion of the $1 \times 1$ phase, the $3 \times 3$ phase appears ($t = 1500$ s, marked “C”). The associated µLEED pattern is shown in Fig. 1(c). This pattern corresponds to a superposition of diffraction from a graphene lattice and diffraction from a $3 \times 3$-SiC(0001) surface. For example, the hexagonal array of spots near the (0,0) beam arise from (4/3,2/3) diffraction from the SiC lattice and by (0,1) diffraction from the graphene lattice. The strong “double diffraction” shows that the $3 \times 3$ phase is coincident with the graphene. The nucleation of the $3 \times 3$ phase is very different from that $1 \times 1$ phase. In contrast to the $1 \times 1$ phase, which nucleates at the edges of graphene domains and grows inward, the $3 \times 3$ phase nucleates homogeneously, with many small domains that coalesce. Eventually, all of the graphene regions have the $3 \times 3$ structure. With continued exposure to disilane, no further change in the surface structure is observed, implying that the $3 \times 3$ phase is self-limiting. This is reminiscent of the $3 \times 3$ phase of the clean SiC(0001) surface, which also self-limits in this temperature and pressure range. On the clean SiC(0001) surface, there is also a transition from a low-coverage $1 \times 1$ phase to a higher-coverage $3 \times 3$ phase. $^{6}$

A sequence of images recorded during intercalation under a complete buffer layer is shown in Fig. 3. The starting surface (Fig. 3(a)) consists of a complete buffer layer with a small amount of “1 ML” graphene at the step edges. Growth of the $1 \times 1$ phase during exposure to disilane is shown in Fig. 3(b). As described above, the growth of the $3 \times 3$ phase proceeds rapidly when there are open SiC areas on the substrate. However, for the case of the complete buffer layer, once the intercalated $1 \times 1$ phase forms, the intercalation rate appears to drops significantly. After completion of the $1 \times 1$ phase (Fig. 3(c)), a complex sequence of diffraction patterns are observed, corresponding to structures with incommensurate or very large unit cells. Similar patterns are observed on clean SiC(0001) at intermediate Si coverages between those of the $1 \times 1$ and $3 \times 3$ phases. In analogy, it is likely that the complex intercalated structures we observe correspond to Si coverages larger than that of the $1 \times 1$ phase, but insufficient to form the $3 \times 3$ phase. It may be that a significant Si supersaturation is needed to drive the complete formation of the $3 \times 3$ phase. The efficient decomposition of disilane that characterizes SiC(0001) is unlikely to take place on graphene, which may explain the difficulty in reaching the $3 \times 3$ intercalated structure for a fully closed buffer layer.
Due to strong interaction with the SiC substrate, the buffer layer band structure does not have the characteristic π-bands of graphene. If intercalation decouples the buffer layer, the π-band structure characteristic of free-standing graphene will be restored. Virojanadara et al.12 and Xia et al.13 used direct measurement of the band dispersion near the Dirac point to monitor the decoupling in two-layer films (buffer layer plus an additional graphene layer). When the buffer layer is decoupled, a second set of bands is observed at the K point, characteristic of bilayer graphene. Here, we use an alternate approach based on plasmon loss spectroscopy.11,19 The band structure of graphene gives rise to a characteristic π-plasmon with an excitation energy of 5–6 eV.20,21 However, the π-bands of the buffer layer are disrupted by covalent bonding to the substrate, and this plasmon is not observed.

If the incident electron energy in LEEM is higher than the plasmon energy, a fraction of the incident electrons in LEEM will scatter inelastically, exciting plasmons in the graphene layer. We performed in situ electron energy loss spectroscopy (EELS) measurements, using the in-line energy filter, to detect the excitation of graphene plasmons by energy-analyzing the reflected electrons.17 EELS spectra recorded from the buffer layer before Si exposure (black), 1 × 1 phase (red), and 3 × 3 phase (blue) are shown in Fig. 4(a). The incident electron energy was 33 eV and the scattering geometry was close to specular, with near-normal incidence and reflection. The spectrum from the 6√3 (coupled) buffer layer is featureless except for a rise in the background above 25 eV energy loss due to secondary electrons. Specifically, there are no loss features near 6 eV. The spectra from the 1 × 1 and 3 × 3 phases are very different. In addition to the secondary tail, there is a clear loss feature at 6 eV, corresponding to the π-plasmon of graphene. The existence of this feature shows that the graphene π-bands have been restored by the formation of the 1 × 1 and 3 × 3 phases. That is, both phases correspond to decoupled graphene.

Ex situ Raman spectroscopy also shows that 1 × 1 and 3 × 3 phases decouple the buffer layer. Raman spectra highlighting the 2D feature are shown in Fig. 4(b). The spectrum from the 6√3 buffer layer is featureless in this region, again indicating strong coupling to the SiC substrate. A spectrum from monolayer graphene (coupled buffer-layer and one additional graphene layer) shows a strong 2D peak at 2724 cm⁻¹. Both the 1 × 1 and 3 × 3 phases exhibit strong 2D features, at 2671 cm⁻¹ and 2639 cm⁻¹, respectively, confirming the decoupling of the buffer layer in these intercalated structures. The 2D peaks are shifted to lower frequency, which may indicate n-doping of the buffer layer by the intercalated silicon.22 The shift may also indicate a change in the graphene layer strain. However, the red shift of the 2D band would correspond to the development of a significant tensile strain in the graphene upon intercalation,23,24 which is, perhaps, unlikely. It is noteworthy that the frequencies are lower than those measured for either epitaxial graphene25 or CVD graphene (Fig. 4(c)) transferred to SiO₂. Since the Raman measurement was made in air, this suggests that the oxidation of the intercalated phases under ambient conditions.

**FIG. 4.** Spectroscopy of the intercalated Si structures. (a) **In situ** EELS spectra recorded from the buffer layer before intercalation (dashed curve) and from the 3 × 3 structure after intercalation (solid curve). The appearance of a strong π-plasmon loss feature at 6 eV indicates that the graphene in the 3 × 3 phase is decoupled from the substrate. The incident electron energy was 33 eV. (b) Comparison of the **ex situ** Raman 2D-band intensity of the 3 × 3 and 1 × 1 Si structures with those of monolayer graphene on SiC(0001), the 6√3 graphene buffer layer before intercalation, and monolayer graphene grown by CVD and transferred to SiO₂. The presence of a strong 2D-band feature indicates that the 3 × 3 and 1 × 1 structures both decouple the buffer layer from the substrate.
conditions proceeds extremely slowly. That is, the $3 \times 3$ phase is electronically very different from SiO$_2$.

In summary, we have demonstrated an integrated disilane annealing process for creating a single, decoupled graphene layer on SiC(0001). Surface cleaning, buffer layer formation, and self-limiting silicon intercalation are all carried out in single process with a modest disilane pressure of $10^{-6}$ Torr. Two intercalated Si phases are identified, a $1 \times 1$ phase that appears to be similar to that identified by Xia et al.,$^{13}$ and $3 \times 3$ phase at higher silicon coverage. EELS and Raman spectroscopy measurements show that both phases decouple the buffer layer from the SiC substrate. This process presents a significant simplification of epi-graphene synthesis at much reduced pressures and substrate temperatures.