Controllable poly-crystalline bilayered and multilayered graphene film growth by reciprocal chemical vapor deposition†

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We report the selective growth of large-area bilayered graphene film and multilayered graphene film on copper. This growth was achieved by introducing a reciprocal chemical vapor deposition (CVD) process that took advantage of an intermediate h-BN layer as a sacrificial template for graphene growth. A thin h-BN film, initially grown on the copper substrate using CVD methods, was locally etched away during the subsequent graphene growth under residual H2 and CH4 gas flows. Etching of the h-BN layer formed a channel that permitted the growth of additional graphene adlayers below the existing graphene layer. Bilayered graphene typically covers an entire Cu foil with domain sizes of 10–50 µm, whereas multilayered graphene can be epitaxially grown to form islands a few hundreds of microns in size. This new mechanism, in which graphene growth proceeded simultaneously with h-BN etching, suggests a potential approach to control graphene layers for engineering the band structures of large-area graphene for electronic device applications.

Introduction

A major breakthrough toward realizing industrial applications of graphene has been made using chemical vapor deposition (CVD) methods.† Graphene films 30 inches in width can be produced using a roll-to-roll process in a CVD system.‡ Multilayered graphene grown on a platinum surface using CVD methods can yield a carrier mobility up to 7100 cm2 V−1 s−1, comparable to the mobilities obtained from exfoliated graphene mounted on SiO2/Si.† Recently, another type of CVD graphene was grown directly on h-BN/Cu substrates, followed by a study of the catalytic growth mechanism.¶,‡ The application of monolayered graphene to electronic devices remains limited, however, by graphene’s unique zero band gap dispersion relation.¶ Luckily, the band gap of AB-stacked bilayered graphene may be tuned under an electric field or using chemical conjugation.¶,¶ Systematic growth and study of bilayered graphene films, however, has not been enough, although a variety of CVD studies have been applied to high-quality monolayered graphene with large domain sizes and few or no grain boundaries.¶–12 Here, we report a unique method for the selective growth of a multilayered graphene and a poly-crystalline bilayered graphene (pBLG) film with a typical domain size of ∼50 µm. This growth was achieved by introducing a reciprocal CVD process that took advantage of an intermediate CVD h-BN film as a sacrificial template for graphene growth. This new method suggests a high potential for graphene with a controllable number of layers for graphene-based science and device applications.

Experimental

Chemical polishing of Cu

A Cu foil from Alfa Aesar (no. 13382) was used as the growth substrate and was cut into pieces 3 × 5 cm in size. The Cu foil was then chemically polished in a solution containing 20 g potassium persulfate, 98%, and 500 mL DI water under an applied current of 0.6 A for 10 min to remove impurities and the native oxide. The Cu foil was then rinsed with HF (20%) three times to remove the etchant residue. Finally, the foil was dried under N2 gas.
Growth of the h-BN and graphene layers

A large area h-BN film, which acted as a sacrificial template during multilayered/bilayered graphene growth, was grown on the Cu foils (prepared as described above) using LP-CVD methods (with a pressure of 7 mTorr), as reported previously. A borazine source was introduced into the chamber along with the N₂ carrier gas at 1050 °C. The thickness of the h-BN layer could be controlled according to the h-BN growth time: h-BN films of the monolayer, 2 nm or 5 nm thick were grown over 25 min, 40 min or 60 min, respectively, as shown in Fig. S2.† The thickness and surface uniformity were confirmed by AFM as shown in Fig. S3 and S4.† After the h-BN film had been deposited, graphene was CVD-grown under 5 sccm H₂ and 0.5 sccm CH₄ for 12 hours at 1050 °C. Fig. S1(a)† illustrates the layer growth process in detail, and Fig. S1(b)† lists the different conditions used during the graphene growth step to produce graphene/h-BN heterostructure growth and epitaxial multilayered graphene growth.

Transfer of graphene

Each graphene layer was transferred from the Cu foil to other substrates (SiO₂/Si, quartz, or a Si₃N₄ TEM grid) by spin-coating a 950PMMA A6 (Microchem) supporting scaffold onto the graphene surface with a spin speed of 45 000 rpm for 55 seconds. The sample was then cured by heating on a hot plate at 90 °C for 5 minutes. The underlying Cu was etched away using an iron(III) chloride solution (with a concentration of 0.1 g mL⁻¹) over 12 hours. The PMMA/graphene film was rinsed twice in deionized water and once in HCl (0.3 g mL⁻¹) for 10 minutes to remove residual iron(III) chloride. The film was then rinsed again in deionized water. Finally, the sample was transferred onto the target substrate. After the sample had been transferred and dried, the PMMA was removed by heating in acetone (on a hot plate at 52 °C) for three minutes.

Characterization

X-ray photoelectron spectroscopy (XPS) studies were carried out on an ESCA Lab2201-XL spectrometer using an Al Kα X-ray excitation source. The structure and crystallinity were characterized using a transmission electron microscope (TEM 2100F, JEOL) equipped with a selected-area electron diffraction (SAED) instrument. A laser micro-Raman spectrometer (Kaiser Optical System Model RXN1, 532 nm excitation wavelength) was used into the gap to form a graphene adlayer beneath the first graphene layer (the top-most layer). Once the Cu surface becomes fully covered with the first graphene layer, the graphene adlayers ceased their growth beneath the first graphene layer, as shown in Fig. 1(b) and (c). The parameters that governed graphene/h-BN growth (Fig. 1(a)) and multilayered graphene growth (Fig. 1(b)) are discussed in the ESI (Fig. S1†).

Optical microscopy (OM) images shown in Fig. 1(b) reveal that the multilayered graphene islands were formed with tens of microns in size. Careful observations revealed that the edge angles of the different graphene layers within a given graphene island (intra-island angles) were perfectly (100%) parallel between the 3rd layer and the higher-index layers. Only the edge angles (>93%) between the 2nd and 3rd layers were not universally parallel (see Fig. S6 in the ESI†). As the fully covered top graphene layer (mother layer) was shared by all of the multilayered graphene islands, the edge angles of the adjacent graphene islands (inter-island angle) were mainly 0° and 60°, with a small distribution of angles near 30° and 85° (see Fig. S7 in the ESI†). Finally, the process was further optimized using one atomic monolayer of CVD h-BN to synthesize a bilayered graphene film, as shown in Fig. 1(c). The h-BN etching process played a critical role in forming bilayered or multilayered graphene. Three different thicknesses of the h-BN layer (5 nm, 2 nm, or 1 atomic layer, which are grown by controlling the growth time are shown in Fig. S2†) were used as a template. Fig. 2(a)–(c) show the OM images of graphene grown on each h-BN layer, revealing very different size and thickness distributions of graphene islands. The graphene layer grown using a 5 nm thick h-BN film yielded the largest number of layers, although the island areas were small.

Results and discussion

When combined with the in situ CVD growth of a graphene/h-BN film, an intermediate empty gap could be formed by etching the initial h-BN layers to enable the controlled CVD growth of additional graphene layers as shown in Fig. 1. A thin h-BN film, initially grown on the copper substrate by CVD, provided a sacrificial template that will be slowly etched away during the subsequent graphene growth by residual hydrogen atoms present in the H₂ gas flow or produced by the decompo-
Fig. 2 The thickness of the h-BN layer in the reciprocal CVD process determined the properties of the resulting graphene layer. (a)–(c) OM images of graphene grown using h-BN films 5 nm, 2 nm, or 1 monolayer thick, respectively. The inset of (a) shows a magnified view of the film, and the inset of (b) shows the areal ratio of each layer compared with the area of the mother (2nd) layer. (d) Shows a histogram of the areal density versus the number of graphene layers present in the samples shown in (a)–(c). (e), (f) The UV-visible absorption spectra and XPS data measured at different growth times confirmed that the h-BN layer had been etched away, and no traces of B or N remained. The scale bars indicate 50 μm in (a)–(c) and 10 μm in the inset of (a).

on a 2 nm thick h-BN layer, however, yielded fewer layers with a larger average area. The inset in Fig. 2(b) shows the growth speed of each layer formed using a 2 nm thick h-BN film. The first graphene layer covered the entire surface and was shared among all graphene islands; therefore, the areal ratio of the third layer up to the tenth layer was compared with the area of the mother 2nd layer. The use of a one atomic monolayered thick h-BN as a template mainly yielded bilayered graphene (>96.7% in Fig. 2(c)). When an h-BN monolayer was used as a sacrificial film, therefore, the gap thickness between a Cu surface and the first graphene layer was about ∼0.35 nm. This gap thickness is not enough to grow many layers of graphene, as indicated in Fig. 2(d) that the bilayered graphene covers >96.7% of the surface. The key for this is, we think, the larger domain size of the h-BN monolayer, which reduces the number of nucleation seeds. The less number of nucleation seeds for h-BN as well as (in situ) sequential and slow CVD process for graphene can grow a polycrystalline bilayered graphene film having very large coverage. To compare, we had also grown graphene on a bare copper substrate with the same growth conditions and found out that in this case we can only obtain monolayered graphene, as shown in Fig. S5.† The number of CVD graphene layers could be controlled by using an h-BN film with a well-defined thickness as a sacrificial spacer and growth template. Even bilayered graphene films could be intentionally grown.

The complete etching of the initial h-BN layer with only graphene was confirmed using UV-visible absorption spectroscopy and XPS measurements of the samples with different growth times of reciprocal CVD. Fig. 2(e) shows the UV-visible absorption spectroscopy data obtained after 0, 0.5, 0.75, 1.0, 1.5, or 2.0 hours of graphene growth. The spectrum collected from the initial sample without graphene (black color) revealed a very high and sharp h-BN peak at 201 nm, indicating the presence of the high quality h-BN film.14 As the graphene growth time increased, the h-BN peak became smaller and broader and finally disappeared completely after one hour of graphene growth. The graphene peak at 265 nm appeared after 0.5 hours and continued to grow with time.4 The etching of the h-BN layer was further verified using XPS techniques by measuring the B and N elemental compositions of the same samples (Fig. 2(f)). The peaks corresponding to B and N disappeared completely after 2 hours of graphene growth. All the studies presented in Fig. 2(e) and (f) were performed using the multilayered graphene shown in Fig. 2(b) (2 nm thick h-BN). Themodel for graphene growth by a reciprocal CVD process is illustrated in Fig. S9, and Fig. S10† shows the details about bilayer and multilayer growth cases.

The multilayered graphene films were carefully examined for quality using confocal Raman spectroscopy and transmission electron microscopy (TEM). A graphene island with more than seven layers thick was intentionally selected. Fig. 3(a) shows a series of Raman spectra corresponding to high-quality graphene. The intensity height, peak position, and G-to-2D peak ratio in the Raman spectrum depended on the number of graphene layers present.15 The epitaxy of the multilayered graphene was characterized by measuring the 2D and G peaks positions, the 2D/G peak height ratio, and the full width at half maximum (FWHM) of the 2D peak. The 2D peak position was located at 2671.7 cm\(^{-1}\) for the monolayered
graphene, and a blue shift was observed upon the addition of more layers (black curve in Fig. 3(b)). The G peak position displayed a red shift from 1576.1 cm$^{-1}$ (monolayer), and quickly reached a maximum of 1569.5 cm$^{-1}$ at the fourth layer (red curve in Fig. 3(b)). Fig. 3(c) shows a high 2D/G peak ratio of 1.77 and a sharp 2D peak with a FWHM of 40.26 cm$^{-1}$ for monolayered graphene. As the number of graphene layers increased, the 2D/G peak height ratio decreased to 0.76 for the bilayer and reached a maximum at the fourth layer. The 2D peak width increased rapidly and reached a maximum at the fourth layer. Fig. 3(d)-(f) show Lorentzian curve fits of the 2D peaks corresponding to monolayered, bilayered, or trilayered graphene, respectively, with the fit parameters obtained from each sample. The Raman spectral features also agreed well with previous studies of epitaxial graphene flakes that were mechanically exfoliated from HOPG. Epitaxial growth on graphene, respectively, with the fit parameters obtained from the atomic scale was confirmed using TEM measurements and high-resolution electron diffraction (SAED) measurements. Fig. 3(g) shows a well-defined angle of 120° at one corner of the higher-index layer. Fig. 3(h) and (i) show the SAED data obtained from two different layers (red and yellow circles). These data were consistent with the crystallinity corresponding to AB stacking. Multilayered graphene was confirmed to have grown epitaxially by a reciprocal CVD process involving simultaneous graphene growth and h-BN etching.

Fig. 4(a) is an OM image of a bilayered graphene film and Fig. 4(b) and (c) show a two-dimensional Raman mapping of the G band and 2D band. Although >96.7% of the entire sample area was covered with bilayered graphene, the G band and 2D band mapping revealed sharp domain boundaries with allowing only a few discrete contrasts. The intensity of the Raman G band could be strongly enhanced at the twisted angle (at 12.5°) of the bilayered graphene, when a laser excitation energy of 2.33 eV is used, due to a singularity in the joint density of states of the twisted bilayered graphene (tBLG). The area, width, and position of the 2D band as well as the 2D/G ratio also depended on the twisted angle. The results suggested that the entire bilayered graphene film was not pure bilayered graphene of an AB stacking structure, but rather poly-crystalline with a few selected twisted angles with very sharp boundaries. The domains of a poly-crystalline bilayered graphene (pBLG) film are characterized by the twisted angle between layers, and not by the structural boundary of the top layer only. A typical domain size in a bilayered graphene film (as defined by twisted angles) can be smaller than the corresponding value in monolayered graphene (defined by the structural boundaries). In our work, the maximum domain size of the poly-crystalline bilayered graphene was found to be ∼50 µm.

High-resolution TEM and SAED measurements were collected from the poly-crystalline bilayered graphene. Fig. 4(d)-(f) and (j)-(l) show the atomic-resolution TEM images, and Fig. 4(g)-(i) and (m)-(o) present the corresponding electron diffraction data. Fig. 4(g) reveals variations in the peak intensities, as indicated by the yellow and red circles, suggesting that Fig. 4(d) corresponds to a bilayer having an AB stacking structure. The diffraction pattern and intensities shown in Fig. 4(h) indicate that Fig. 4(e) corresponds to AA stacking. Fig. 4(f), (j), (k), and (l) present the dimensions of the Moiré patterns produced by the twisted angles of the poly-crystalline bilayered graphene. Twisted angles of 7°, 15°, 20°, and 29° were measured from the corresponding SAED data. These twisted angles in a poly-crystalline bilayered graphene match well with commensurate rotations between two graphene layers. In a few cases, twisted trilayers were observed (see Fig. S12 in the ESI†). Additionally, more than 30 field effect transistor (FET) devices were prepared using poly-crystalline bilayered graphene films with channel sizes of 20 µm × 10 µm. These device measurements were consistent with the characteristics of bilayered graphene (see Fig. 5). Further optimization of
h-BN layer quality on Cu substrates, therefore, can be applied to improve the domain sizes and the twisted orientations of the bilayered graphene on a large scale.

Conclusions

In conclusion, poly-crystalline bilayered graphene and multilayered graphene were grown on Cu substrates using a reciprocal CVD process in which graphene was grown while an h-BN layer was simultaneously etched away. During graphene growth on the h-BN/Cu substrate under optimized conditions, residual hydrogen atoms present in the H2 gas flow or produced by the decomposition of CH4 etched away the h-BN film to enable the growth of an additional graphene layer. UV-visible absorption spectroscopy and XPS measurements confirmed that the h-BN buffer layer was etched away completely. The domain sizes and structures of the epitaxial multilayers and poly-crystalline bilayers of graphene were studied using confocal Raman spectroscopy and TEM/SAED methods. The reciprocal CVD process involving simultaneous graphene growth and h-BN etching constitutes a significant advancement for controlling the number of CVD graphene layers for graphene-based science and device applications.

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Notes and references