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A simple method to tune graphene growth between monolayer and bilayer

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Selective growth of either monolayer or bilayer graphene is of great importance. We developed a method to readily tune large area graphene growth from complete monolayer to complete bilayer. In an ambient pressure chemical vapor deposition process, we used the sample temperature at which to start the H₂ flow as the control parameter and realized the change from monolayer to bilayer growth of graphene on Cu foil. When the H₂ starting temperature was above 700°C, continuous monolayer graphene films were obtained. When the H₂ starting temperature was below 350°C, continuous bilayer films were obtained. Detailed characterization of the samples treated under various conditions revealed that heating without the H₂ flow caused Cu oxidation. The more the Cu substrate oxidized, the less graphene bilayer could form. © 2016 Au-thor(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4943040]

INTRODUCTION

In addition to the fascinating monolayer graphene, bilayer graphene has attracted increasing attention. AB-stacked bilayer graphene shows a tunable band gap in a vertical electric field.^{1,2} This makes it applicable in devices such as field effect transistors. On the other hand, twisted bilayer graphene also exhibits interesting physics such as the twist-dependent Van Hove singularity.^{3,4}

Bilayer graphene can be prepared by mechanical exfoliation of graphite.⁵ However, this method is unsuitable for mass production. Chemical vapor deposition (CVD) growth on metals has been another important method to make bilayer graphene.^{6–29} Graphene grown on nickel is usually multilayer because of the high solubility of carbon in Ni. In contrast, graphene grown on copper is typically monolayer due to the "self-limiting" effect³⁰ Cu-Ni alloy has been used to grow bilayer graphene^{6–8} by carefully adjusting the atomic percentage. Recently, researchers have also grown bilayer graphene on copper by regulating various conditions including the carbon source,^{9,10} copper purity,^{11,12} pressure,¹³ growth temperature¹⁴ and gas flow rate.¹⁵ However, these methods either require much prolonged growth processes or produce bilayer films which are not continuous because the second layer is much smaller than the first. Meanwhile, these recipes for bilayer growth are quite different from those for monolayer and usually require different setup. Therefore, high yield growth of continuous bilayer graphene films remains a topic of intensive research efforts.



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Here we report an ambient pressure chemical vapor deposition (APCVD) process with the capability to tune from monolayer growth to bilayer growth. We used the sample temperature at which to start the H_2 flow as the sole control parameter. The obtained samples were characterized by optical microscopy, Raman spectroscopy, scanning tunneling microscopy (STM) and scanning electron microscopy (SEM). It was revealed that annealing the sample without the H_2 flow will increase the degree of Cu oxidation and consequently inhibit the formation of a second graphene layer.

EXPERIMENT

Graphene samples were grown on copper foils (127 μ m thick, 99.9%, Alfa Aesar) in a furnace by an APCVD process as schematically shown in Figure 1(a). The furnace was closed but not air sealed or pumped. The Cu foils were heated from room temperature to 1050 °C with Ar and H₂ flow of 500 sccm and 20 sccm, respectively. The temperature was kept at 1050 °C for 40 minutes or longer. The Ar flow was on during the whole process. The starting temperature of the H₂ flow was varied as the control parameter. The other conditions were kept the same. The growth process lasted for 20 minutes with an Ar/H₂/CH₄ flow rate of 500 /20/ 10 sccm. After growth, the samples were cooled naturally to room temperature in about 4 hours with the Ar /H₂ flow on.

Raman spectra were taken by a Renishaw inVia system with the excitation wavelength of 514 nm. Optical images of graphene on Cu were taken by an Olympus microscope (Olympus BX51). STM and STS measurements were carried out in a UNISOKU UHV STM system at 77 K with a base pressure below 3×10^{-7} Pa. SEM measurements were carried out in a FEI Helios NanoLab 600i system.



FIG. 1. Growth of monolayer and bilayer graphene. (a) Schematic diagram of the APCVD process. The whole process includes four steps: heating up, annealing, growth, and cooling down. The dark yellow and orange lines correspond to the synthesis of complete monolayers and complete bilayers, respectively. The flow rates (when switched on) of Ar, H₂ and CH₄ are 500, 20 and 10 sccm, respectively. (b, c) Optical images of the monolayer and bilayer samples, respectively. The scale bar is 400 μ m. (d) Raman results. Points measured all over the surface of the samples give consistent characteristics. For the bilayer samples, I_{2D}/I_G~0.8, the FWHM of the 2D band is 55-65 cm⁻¹. For the monolayer samples, I_{2D}/I_G~2.2, the FWHM of the 2D band is 33-41 cm⁻¹. (e, f) Lorentz curve fitting of the 2D band of the monolayer and bilayer samples, respectively. The green curve in (d) is one Lorentz fit with the FWHM of 34 cm⁻¹. The green curves in (f) are four Lorentz curves with the FWHM all of 34 cm⁻¹.

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RESULTS AND DISCUSSION

Figure 1(b) and 1(c) show the typical optical micrographs of the samples prepared with the H_2 flow starting at 1050 °C (samples S1050) and room temperature (samples S25), respectively. As it turned out, S1050 and S25 are uniform monolayer and bilayer graphene films, respectively.

To characterize the quality and layer number of the graphene samples, we have performed Raman spectroscopy measurements. Figure 1(d) shows representative Raman spectra for S1050 and S25 samples with the excitation wavelength of 514nm. The two peaks around 1590 cm⁻¹ and 2700 cm⁻¹ correspond to the Raman G band and 2D band of graphene,^{31,32} respectively. The intensity ratio of the 2D band and G band I_{2D}/I_G for S1050 (the dark yellow curve) is 2.2 and the full width at half-maximum (FWHM) of the 2D band is 37 cm⁻¹. These are characteristics of monolayer graphene.^{13,27} For S25 (the orange curve), I_{2D}/I_G is 0.83 and the FWHM of the 2D band is 60 cm⁻¹, characteristics of bilayer graphene.^{13,27} The negligible D band around 1350 cm⁻¹ in both curves indicates low defect density and high quality of the graphene samples.

Further analysis of the spectra reveals that the 2D band of S1050 can be well fitted by a single Lorentz curve (Figure 1(e)) while that of S25 cannot. Instead, Figure 1(f) shows that the 2D band of S25 can be excellently fitted (shown in orange curve) with four Lorentz curves, whose FWHM are all 34 cm^{-1} (shown in green curves). This verifies that S25 are indeed bilayer graphene samples.^{14,17,26,31}

Raman mapping was used to check the uniformity of the above monolayer and bilayer samples and the I_{2D}/I_G results are shown in Figure 2(a) and 2(b). Figure 2(a) corresponds to monolayer samples S1050. The I_{2D}/I_G value is larger than 2 all over the surface. In addition, the FWHM value of the 2D band is ~30 cm⁻¹. These mapping results show that more than 98% of the surface of the S1050 samples is covered by monolayer graphene. Figure 2(b) corresponds to bilayer samples S25. The I_{2D}/I_G value is mostly between 0.7 and 1.3. The FWHM value of the 2D band is mostly between 45 cm⁻¹ and 65 cm⁻¹. These mapping results indicate that more than 95% of the surface of the S25 samples is covered by bilayer graphene. The uniformity of the samples shows that our method can be used for high yield selective growth of monolayer or bilayer graphene.



FIG. 2. Raman mapping and STM results of the monolayer and bilayer samples. (a) I_{2D}/I_G for a typical monolayer sample. The ratio is larger than 2 all over the surface. (b) I_{2D}/I_G for a typical bilayer sample. The ratio is ~ 1.0 and quite uniform. The excitation wavelength is 633 nm. (c) Atomic resolution STM of an AB stacked area. Only one sublattice is visible. Inset: The corresponding FFT. (d) STM of a twisted bilayer area. Both sublattices are visible. (e) Typical STS results of the samples. The K-point energy is quite close to the Fermi level, indicating little doping in graphene. (f) A larger twisted bilayer area with a moiré pattern that corresponds to a twist angle of 2.9°. Right inset: FFT. The outer hexagon spots correspond to the atomic lattice. Left inset: Zoom-in of the inner hexagon (yellow square) in the FFT, which corresponds to the moiré pattern. Tunneling set points: -100 meV bias and 200 pA current. The measurements were conducted at 77K in UHV.

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Next, the stacking order of the bilayer samples was checked. Since the I_{2D}/I_G value is ~1, most area should be AB stacked, not twisted.^{6,13,14} Results of scanning tunneling microscopy (STM) measurements are consistent with the Raman results. Most area is AB stacked as shown in the typical STM image and its Fast Fourier Transform (FFT) result in Figure 2(c). Only one sublattice of graphene shows up in the image, a consequence of Bernal stacking.^{6,33,34} As comparison, both sublattices are visible on twisted bilayer graphene (Figure 2(d)). The K-point energy in the scanning tunneling spectrum (STS) results in Figure 2(e) is within 50 meV of the Fermi level. This indicates little doping of the graphene samples, consistent with the Raman results. Occasionally twisted bilayer area was also found. Figure 2(f) shows the STM image of such an area with a Moiré pattern caused by the twist between the layers.

So, just by changing the temperature at which we turn on the hydrogen gas flow during the heat-up process, we can selectively grow continuous monolayer or bilayer graphene films by APCVD. If we start the H₂ flow at room temperature, bilayer graphene is obtained. If we start the H₂ flow at 1050 °C, monolayer graphene is obtained. At first thought, maybe the difference is due to the total time duration of the H₂ flow? We started the H₂ flow at 1050 °C and annealed the Cu foil for 1hr longer to compensate for the total H₂ flow time. Still monolayer graphene was obtained. So the decisive factor should be the starting temperature (not the time duration) of the H₂ flow.

Next we have done a series of growth experiments with the H₂ starting temperature in the range between 25 °C (room temperature) and 1050 °C to check at which value the transition (from monolayer to bilayer growth) occurs. Figure 3(a) shows the typical Raman spectra of these samples. When the H₂ starting temperature is above 700 °C, continuous monolayer graphene is grown



FIG. 3. (a) Raman spectra of graphene samples. The H₂ flow was turned on at different temperatures. The spectra are vertically displaced for clarity. When the H₂ starting temperature was lower than 350 °C, the I_{2D}/I_G ratio is ~ 1.0 all over the surface, and the FWHM of the 2D band is ~60 cm⁻¹, suggesting continuous bilayer graphene films. When the H₂ starting temperature was higher than 700 °C, the I_{2D}/I_G ratio of >2.2 and the 2D band FWHM of ~40 cm⁻¹ indicate continuous monolayer graphene. When the H₂ starting temperature was between 400 °C and 600 °C, there are both monolayer and bilayer regions. (b) Optical image of a graphene sample with the H₂ flow turned on at 550°C. The dark and light areas are bilayers and monolayers, respectively. The scale bar is 40 µm. (c) STM image of a graphene step in the sample shown in (b). The step height is 0.35 nm. Multilayer graphene was not found by STM. (d, e) Optical images of the copper foil before and after the heating process (without growth), respectively. The heating to 1050 °C and cooling down naturally to room temerature were done in the furnace with an Ar flow of 500 sccm (no H₂ and CH₄). After the process, the surface color changed from bright yellow to dark orange. (f) Raman spectra of the Cu foils shown in (d) and (e). Raman peaks corresponding to Cu₂O emerged after the heating process. No other peaks are discernable. This indicates that oxidation is the major change caused by heating without H₂.

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 $(I_{2D}/I_G > 2.2, 2D \text{ band FWHM } \sim 40 \text{ cm}^{-1})$. When the H₂ starting temperature is below 350 °C, continuous bilayer graphene is grown $(I_{2D}/I_G \sim 1.0, 2D \text{ band FWHM } \sim 60 \text{ cm}^{-1})$. When the H₂ starting temperature is between 400 °C and 600 °C, we find both monolayer and bilayer areas on the surface as shown in Figure 3(b). The darker and brighter areas are graphene bilayers and monolayers, respectively. STM measurements further verified the layer number of the graphene samples. The step height in Figure 3(c) is 0.35 nm, indicating just two layers.

What is the mechanism behind this temperature dependent behavior? It is known that hydrogen can significantly affect graphene's growth and properties.^{13,15,35,36} However, since the H₂ flow conditions were kept the same after the carbon source (CH₄) was introduced, it should be something else that caused the difference between monolayer and bilayer growth. Due to unavoidable outgasing in the furnace at elevated temperatures and air leak during the APCVD process, oxygen exists in the furnace especially when H₂ flow is not on. The Cu foil can get oxidized and affect graphene's growth and properties.^{20,37,38} Recently, people have found that oxygen in Cu can reduce the nucleation density for graphene growth.^{20,37,38} To verify that oxidation is indeed the dominant difference happened to the copper foils, we heated a piece of reference copper foil to 1050 °C in the furnace with only the Ar flow (500 sccm), then turned off the power and cooled to room temperature naturally. The optical micrograph of the copper foil treated this way is shown in Figure 3(e). For comparison, the original Cu foil is shown in Figure 3(f) shows the Raman spectra of the copper foils. Peaks corresponding to Cu₂O³⁹ appear on the heated copper foil but not on the original one.

We believe that the transition from bilayer to monolayer growth is caused by oxygen. With the increase of the H₂ starting temperature, the oxidation of the copper foil gets more severe since the oxidation is a barrier activated process. When the temperature reaches a certain value (400 °C ~ 600° C), the lattice diffusion mode of the oxygen atoms in Cu₂O is activated in addition to the the grain boundary diffusion mode, resulting in a sharp increase of the oxidation rate⁴⁰ and the oxygen solubility in Cu.^{41,42} Oxygen in Cu will then hinder the carbon diffusion and nucleation, effectively inhibit the formation of a second layer.⁴³



FIG. 4. SEM results of the synthesized graphene samples with the H_2 flow switched on at different temperatures. (a) A typical bilayer sample. The H_2 flow was started at room temperature. (b) A sample covered by both monolayer and bilayer (dark) areas (roughly 50/50). The H_2 flow was started at 550 °C. (c) A sample covered by both monolayer and bilayer areas with the bilayer areas reduced to below 10%. The sample was annealed at 550 °C for additional 2 hrs before the H_2 flow was started. (d) A typical monolyer sample. The H_2 flow was started at 1050 °C.

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To further investigate this effect, the substrate was heated to 550°C and maintained there for various periods of time to allow various degrees of Cu oxidation. Then the H₂ flow was turned on and the Cu foil was further heated to 1050 °C. Other conditions were kept the same as in the normal growth process (Figure 1(a)). Figure 4 shows the SEM results of the samples. The starting temperatures of the H₂ flow for the samples in Figure 4(a), 4(b), 4(c), 4(d) were 25 °C, 550 °C, 550 °C and 1050 °C, respectively. The sample in Figure 4(a), 4(b), 4(c), 4(d) have increasing Cu oxidation. And there is a clear trend of decreasing bilayer formation (the darker areas). In fact, additional 2 hrs of oxidation at 550 °C (annealing without the H₂ flow) can efficiently reduce the bilayer area to < 10% as shown in Figure 4(c). Because the oxidation rate at higher temperatures (>700 °C) are exponentially higher, even a few minutes without the H₂ flow will result in the absence of bilayer. This explains the transition from bilayer to monolayer growth quite well.

SUMMARY

We developed a method to readily tune large area graphene growth between monolayer and bilayer. Using the starting temperature of the H_2 flow in an ambient pressure CVD process as the single control parameter, we observed the change from monolayer to bilayer growth on Cu foil. When the H_2 starting temperature was above 700°C, continuous monolayer graphene films were obtained. When the H_2 starting temperature was below 350°C, continuous bilayer films were obtained. Detailed Raman and SEM study of samples treated under various conditions revealed that Cu oxidation played a crucial role in this change. This effect can be well understood since Cu oxidation will inhibit carbon diffusion thus also the formation of a second graphene layer.

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