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Large-area bilayer graphene synthesis in the hot filament chemical vapor deposition reactor

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ABSTRACT

We fabricated large area bilayer graphene by hot filament chemical vapor deposition (HFCVD) on Cu foil. The HFCVD technique can represent a significant advantage over other techniques for industrial scaling at low cost. We performed systematic experiments to determine the best parameters to obtain uniform graphene coverage over an area of ~16 cm^2. The experimental growth parameters are grouped into two distinct regions according to the products obtained: (A) continuous bilayer graphene with low defect density and (B) continuous bilayer graphene with high defect density. The optimum graphene films obtained are uniform bilayer with low defect density, greater than 90% transmittance in the visible region, and no gaps. The high quality of the bilayer graphene was confirmed by Raman spectroscopy mapping. The results show that the ratio of 2D to G peak intensities (I_{2D}/I_G) is in the 0.9–1.6 range over 90% of the area. Moreover, we employed the static cling property of polyethylene terephthalate (PET) to preserve the integrity of the as-grown graphene films in the transfer process, showing that the graphene films become well attached to the SiO_2/Si substrates while the PET films were completely peeled off.

1. Introduction

Graphene is a two-dimensional material made of sp^2 bonded carbon atoms [1–3] that exhibits excellent physical and chemical properties that can enable new disruptive technologies in optoelectronics, high-performance devices, flash memory devices, and bio-sensors [4–8]. In particular, due to its high optical transmittance and conductivity, graphene is an excellent candidate for replacing indium tin oxide (ITO) in products that require transparent conductive films, such as touch screen displays, electronic paper, and organic light-emitting diodes. Moreover, graphene, unlike ITO, has outstanding mechanical flexibility and chemical inertness that are important characteristics for next-generation flexible electronic devices.

Thermal chemical vapor deposition (TCVD) is commonly used for the fabrication of large-area graphene [9–12]. It consists of a tube furnace with horizontal flow of gases, such as methane and hydrogen, which react on catalytic metals, such as Ni and Cu. A closely related deposition technique of industrial use is hot filament chemical vapor deposition (HFCVD). Nonetheless, the HFCVD technique can represent a significant advantage over TCVD when it comes to enlarging the deposition area at a lower cost.

Various groups have alleged to achieve large-area graphene growth by HFCVD [13–16]. Of these reports, only Kataria et al. [16] uses the term HFCVD properly; the other three used adaptations of a tube furnace that are not adequately described by the term HFCVD. Kataria et al. [16] demonstrated discontinuous monolayer graphene deposition over an area of 9×17 μm^2 by HFCVD. However, this area is too small for transparent conductive film applications. To further address this issue, we performed systematic experiments to determine the best parameters to obtain uniform graphene coverage over an area of ~4×4 cm^2. Moreover, we made an adaptation of the transfer procedure described by Cheng et al. [17], using the static cling property of polyethylene terephthalate (PET) to efficiently transfer the as-grown graphene films from one substrate to another while preserving their structural integrity in the process.

2. Experimental

Graphene films were grown on Cu foils (Alfa Aesar, 99.8%, 25 μm thick) cut into 16 cm^2 squares. The Cu substrates were cleaned with acetone, acetic acid, isopropanol, deionized water, and then annealed at 1000 °C in 20 Torr of H_2 for 30 min. The HFCVD chamber (Blue Wave) was then filled to a pressure in the range of 20–50 ± 1 Torr with a gas mixture of CH_4 in H_2 in the range of 1–50%. The Cu substrates were heated to a temperature in the range of 700–1000 ± 1 °C, and the rhenium filaments (8 mm above the substrate) were heated to a

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constant temperature of 2300 ± 10 °C. The substrate temperature was monitored with thermocouples and two pyrometers and controlled independently of the filament temperature that was monitored with two pyrometers. Using Re as the filament material represents a significant advantage as it avoids many of the complications, contamination and downtime associated with W and Ta filaments. Experiments were done for 5, 10, 20, 30 min deposition times. After each deposition was completed, the chamber was actively cooled at a rate of 50 °C/min until reaching 400 °C and then allowed to cool down by itself from this temperature until room temperature.

A static cling film (100 μm) of polyethylene terephthalate (PET) was firmly attached to the as-grown graphene films on Cu foils. The Cu foils were then etched in iron chloride solution kept at 75 °C for 20 min. Finally, the graphene/PET films were rinsed with deionized water and dried with nitrogen. Once placed on the PET support, the graphene films were ready to be directly studied with different characterization techniques. Some of the graphene films were also transferred onto SiO_2/Si substrates, showing that the graphene films become well adhered to the new substrates while the PET films were completely peeled off.

The Raman spectra were collected in the 1000–3000 cm^{-1} range with a step size of 1.0 cm^{-1} using a scanning micro-Raman system (Thermo Scientific DXR) equipped with a 532 nm laser source and a 50× objective lens. The Raman mappings (area scan mode) were done with a step size of 2.1 μm and collecting Raman spectra for 20 seconds at each point. Optical transmittance spectroscopy measurements were performed using UV-Vis-NIR spectroscopy (Shimadzu UV-3600). A blank PET substrate was used as reference for baseline subtraction. The sheet resistance was measured using the Van der Pauw method. Transmission electron microscopy was done with a high resolution Cs probe corrected JEOL JEM-2200FS TEM. The graphene samples were prepared for TEM by a single transfer onto Quantifoil holey carbon TEM grids with an array of holes of 2 μm diameter.

3. Results and discussion

The results of the systematic experiments performed to grow graphene by HFCDV are summarized in Table 1 in terms of the experimental parameters employed and the Raman features of the corresponding films obtained. The ratio of the intensity of the 2D band to that of the G band is used to determine the number of graphene layers, while the ratio of the intensity of the D band to that of the G is used to determine the degree of disorder in the trigonal carbon network. The experimental growth parameters are grouped into two distinct regions according to the products obtained: (A) continuous bilayer graphene with low defect density and (B) continuous bilayer graphene with high defect density.

The parametric study started with methane concentration variation in the 1–50% range in 5% steps, while keeping the pressure at 35 Torr and the substrate temperature at 850 °C. Graphene growth took place only in the 15–25% CH_4 range. The pressure was then changed in the 20–35 Torr range, and the quality of the graphene films deteriorated as indicated by the D band. Increasing the pressure to 40 Torr yielded amorphous carbon. The substrate temperature was then lowered from 850 °C to 750 °C in steps of 50 °C, resulting in lower graphene quality as indicated by the D band. At temperatures higher that 850 °C, the graphene quality improves and monolayer is achieved, but it grows in discontinuous patches. There appears to be a fundamental tradeoff between continuous–discontinuous coverage and bilayer–monolayer graphene in the HFCVD system. This result is consistent with previous reports [13–16], while expanding the scope of the HFCVD method to encompass the deposition of large area bilayer graphene. From this point forward, we focus our analysis on the structure and properties of the large area bilayer graphene that is obtained in Parametric Region A.

Fig. 1(a) shows the optical image of the large area bilayer graphene transferred onto SiO_2 (300 nm)/Si and PET substrates. It looks transparent and barely noticeable to the naked eye. The transmittance of the HFCVD bilayer graphene films is consistently in the 95–98% range for the 380–1000 nm region. Fig. 1(b) shows the average Raman spectrum measured along a 170 μm line for the HFCVD bilayer graphene on SiO_2/Si substrate (approximately 80 spectra). It contains the D peak at ~1350 cm^{-1}, G peak at ~1582 cm^{-1}, and the 2D peak at ~2695 cm^{-1}. Similar spectra are obtained for graphene on PET. The I_{2D}/I_G ratio is ~1.2 consistent with bilayer graphene [18–20]. However, the assignment of bilayer graphene cannot be unambiguously made based on the I_{2D}/I_G when AB stacking is absent, so an independent characterization technique is required.

Fig. 2a shows the optical image of bilayer graphene single-transferred onto the TEM grid. The high-resolution TEM image of Fig. 2b shows a 8 × 8 nm^2 region of bilayer graphene. The inset contains the corresponding Fast Fourier Transform showing two misoriented hexagons. During TEM observations, most regions of the graphene films generated similar pairs of misoriented hexagons. Hence, the TEM data confirm the bilayer and turbostratic nature the HFCVD graphene.

In order to ascertain the overall homogeneity of the bilayer graphene, we performed Raman spectroscopy scanning and mapping on various places. First, we applied Raman line scan from edge to edge to determine the level of continuity or discontinuity of the bilayer graphene (Fig. 3a). No discontinuities were found, but fluctuations in peaks heights are evident (see 3D view in Fig. 3a). Subsequently, Raman mapping was applied over relatively large areas of approximately 200 × 200 μm^2, in different zones (see Fig. 3c). The green color in Fig. 3c indicates a ratio of 1; for higher ratios, the color shifts to yellow and red; for lower ratios, the color shifts to blue and violet. It is readily seen that the green color dominates the area (about 90%), indicating that the film is for the most part made of bilayer graphene. The rest of the area (about 10%) consists of patches of around 10 × 10 μm^2 or smaller that are either monolayer graphene (yellow/red) or few layer graphene (blue/violet). The whole substrate is uniformly covered without gaps.

Further analysis of the 2D peak reveals that is has a symmetric Lorentzian shape (see Fig. 4). If the bilayer graphene was AB or AA stacked, it would have shown an asymmetric non-Lorentzian shape instead. However, the Lorentzian fit gives an excellent chi square of 0.99. Therefore, the HFCVD bilayer graphene has misoriented or turbostratic layered structure [21–24]. The production of turbostratic bilayer graphene can occur naturally at the surface of crystalline graphite [25] and has also been observed in bilayer graphene grown by TCVD [18].

We performed measurements of the sheet resistance of the HFCVD bilayer graphene films over relatively large areas of 1 cm^2 using the Van der Pauw method. The values found range between 1000 and 5000 Ω/□ (see Fig. 5). These values are compared in Fig. 4 with those reported by other authors for bilayer graphene materials with transmittance values similar to ours. Generally speaking, the sheet resistance values of HFCVD bilayer graphene are about 2–5 times higher than

Table 1
Summary of the systematic parametric study for the growth of graphene by HFCVD.

Parametric region	CH_4 (%)	Pressure (Torr)	Substrate temperature (°C)	Average I_{2D}/I_G	Average I_D/I_G	Result
A	15–25	30–35	800–850	0.9–1.6	0.2–0.3	Continuous bilayer graphene; low defect density
B	15–25	20–30	700–800	0.9–1.1	0.3–0.8	Continuous bilayer graphene; high defect density