Metal-catalyst-free and controllable growth of high-quality monolayer and AB-stacked bilayer graphene on silicon dioxide

Qingfeng Liu, Youpin Gong, Ti Wang, Wai-Lun Chan, and Judy Wu**

Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66045, USA

ABSTRACT

A systematic study shows that continuous graphene with controllable number of layers and stacking structure can be directly grown on SiO₂/Si without any metal catalysts by chemical vapor deposition. Raman spectroscopy and mapping confirm the monolayer, bilayer and few-layer nature of the graphene with a high coverage over ~95 %. Ultraviolet photoemission spectroscopy verifies that the monolayer graphene and AB-stacked bilayer graphene have a work function of 4.46 eV and 4.50 eV, respectively, which are close to that of the intrinsic graphene. This is in contrast to the much lower work function of 4.26 eV observed on Cu-catalyzed graphene probably due to contaminants produced during the transfer process. Field-effect transistors were directly fabricated on graphene/SiO₂/Si for evaluating their electric properties. Importantly, we reveal a crucial role of SiO₂ layer thickness in controlling the graphene structure: (1) monolayer graphene preferably grown on thick SiO₂ layer (~300 nm or higher) by a surface-catalyzed process, and (2) AB-stacked bilayer or few-layer graphene favorably formed on thin SiO₂ layer by a surface-adsorption/precipitation process. This study sheds light on the graphene growth mechanism on SiO₂/Si and this insightful understanding is important to large-scale, controllable CVD growth of graphene in absence of metal catalysts.

*Corresponding author: Email address: qfliu@ku.edu (Q. Liu); jwu@ku.edu (J. Wu)

1. Introduction

Graphene has emerged as an extraordinary two-dimensional material for both fundamental studies and practical applications because of its prominent electrical, mechanical, thermal and optical properties [1-4]. Among many methods developed for fabrication of graphene [5-7], chemical vapor deposition (CVD) has generally been considered to be the most reliable and scalable approach for electronic, photonics and optoelectronics [8, 9]. However, most reported CVD graphene are grown on metals such as Ni and Cu, and thus a cumbersome transfer process has to be required for most subsequent applications. The transfer process typically involves wet etching of the metal catalyst, followed with transfer of graphene onto a target substrate such as SiO₂/Si wafer. Such process is inevitably to damage graphene through introduction of defects (wrinkles, cracks, etc.) and contaminations such as the residual metal impurities and polymer contaminants [10, 11]. Therefore, the direct growth of graphene on dielectric substrates (especially SiO₂/Si) in absence of any metal catalysts is desirable and important to large-scale integration of graphene-based devices. This has motivated an intensive effort recently in exploring metal-catalyst-free growth of graphene on dielectric substrates [12-19]. However, the as-grown graphene on dielectric substrates often has a high and wide D band in Raman spectra [12-19], indicating a considerably lower quality when compared to that of their counterpart grown on metals such as Cu and Ni [8, 9]. Although continuous heterogeneous graphene composed of different layers has been demonstrated on SiO₂ via an oxygen-aided CVD method [18, 19], obtaining large-area uniform graphene on SiO₂ with precisely-controlled layer numbers remains a challenge due to lack of a thorough understanding of the graphene growth mechanism.

Motivated by this, we have carried out a systematic study of metal-catalyst-free growth of graphene on SiO₂/Si in the atmospheric pressure CVD process. Through growth optimization such as growth temperature, H₂/CH₄ flow rates and SiO₂ layer thickness, continuous graphene with precisely-controlled layer numbers of monolayer, AB-stacked bilayer or few layers have

achieved on SiO₂/Si in absence of metal catalysts. Moreover, this study has been revealed that the SiO₂ thickness plays a crucial role in determining the growth modes of graphene through a correlated interaction between SiO₂, Si and C at the SiO₂ surface.

2. Experimental

The synthesis was performed in a quartz tube reactor (25 mm in diameter) inside a horizontal CVD furnace. In a typical experiment, a clean SiO₂/Si substrate of variable SiO₂ thickness of 0, 90, 300 or 500 nm was placed at the center of a quartz tube reactor. H₂ (70-160 sccm) was introduced in the reactor while it was heated up to growth temperatures in the range of 1060-1100 °C. At the growth temperature, CH₄ (30 sccm) was fed into the reactor to initiate the graphene growth on the SiO₂/Si surface. After the growth, the furnace was quickly cooled to room temperature under the protection of H₂. The samples were characterized by using Raman spectroscopy (WiTec alpha300), atomic force microscopy (AFM, Agilent Technologies, Tempe, AZ), ultraviolet photoemission spectroscopy (UPS), X-ray photoemission spectroscopy (XPS, AXISULTRA KRATOS system), and electrical measurements.

The surface work function and valence band structure are measured using UPS. The spectra are measured with electrons emitted along the surface normal direction. Before measurements, each sample is outgassed at 400 °C for 20 hours in a UHV chamber (base pressure: 1×10^{-9} Torr) to ensure the surface cleanliness. The electrical properties of the monolayer and bilayer graphene were characterized by directly fabricating field-effect transistor (FET) on the SiO₂/Si substrates. Ti/Au (2/80 nm) source-drain electrodes were deposited by electron beam evaporation and a graphene stripe with 20 μm width and 10 μm length was formed after O₂ plasma etching. The electrical transport measurements were performed in vacuum using an Agilent B1505A power device analyzer in a probe station.

3. Results and discussion

3.1 Optimization of graphene growth

In order to obtain metal-catalyst-free grown graphene with high quality and controllable layer numbers on SiO₂/Si substrates, it is necessary to systematically study the optimization of the graphene growth. Fig 1a compares Raman spectra of five graphene samples directly grown on SiO₂(500nm)/Si substrates at 1070°C for 7h with different CH₄/ H₂ flow rates (30/70-160 sccm). There are three characteristic peaks of these samples, i.e., the disorder-induced D band (~1350 cm⁻¹), the tangential G band (~1585 cm⁻¹), which is derived from the in-plane vibration of the sp² carbon atoms, and the second-order harmonic 2D band (~2705 cm⁻¹). The single and sharp 2D band and the intensity ratio of 2D band to G bands ($I_{2D}/I_G > 1$) confirm the presence of monolayer graphene, while the 2D band of multilayer graphene can be fitted with multiple peaks, due to the splitting of the electronic band structure of the multilayer material [20-22]. From Fig 1a, it is clearly seen that the H₂ flow rate exerts a significant influence on graphene structure on SiO₂/Si, and that high-quality monolayer graphene growth was realized with over 120 sccm H₂ flow, while the growth of bilayer and few-layer graphene was favored with a lower H₂ flow.

Fig 1b compares the Raman spectra of the graphene grown on SiO₂(500 nm)/Si with a mixed H₂/CH₄ (120/30 sccm) flow at various temperatures ranging from 1065 °C to 1100 °C. In this range, the intensity ratio of D band to G band (I_D/I_G) of the as-grown graphene increases with the decrease of the growth temperature. This indicates that the overall quality of the graphene increases with the decrease of growth temperature. Moreover, monolayer graphene growth is preferred at lower growth temperatures of 1065-1085 °C, while the growth of bilayer and few-layer graphene is favored at higher growth temperature. However, at below 1065 °C of growth temperature, almost no graphene could be directly grown on the SiO₂/Si substrate with all other parameters constant. In contrast, the formation of amorphous carbon is also

concomitantly increasing from the decomposition of methane at over 1090 °C, resulting in a considerable increase of the defect D band and hence degradation of the graphene quality.

Fig. 1 (a-c) Raman spectra (488 nm excitation) of the as-grown graphene (a) with different H_2/CH_4 flow at (b) different growth temperatures on (c) Si substrates with different SiO_2 thicknesses. The spectra are scaled to produce an approximate match in intensity for 2D band. (d) XPS spectra of the $SiO_2(500\text{ nm})/Si$ substrate before and after monolayer graphene growth at 1065 °C for 7 h with a mixed H_2/CH_4 (120/30 sccm) flow.

Especially, the SiO_2 thicknesses on the SiO_2/Si substrates was found to determine both the graphene quality and layer number. Fig 1c compares the Raman spectra of the four graphene samples grown at 1075 °C and a mixed H_2/CH_4 (120/30 sccm) flow on SiO_2/Si with different SiO_2 layer thicknesses of ~0, 90, 300 and 500 nm, respectively. Bilayer graphene is growing on SiO_2/Si with the SiO_2 layer thickness of 90 nm or smaller while monolayer graphene is

obtained on SiO₂/Si with the SiO₂ layer thickness over 300 nm. In both case, the I_D/I_G ratio of the as-grown graphene increases with decreasing SiO₂ thickness. Based on the above analysis, it can be concluded that the metal-catalyst-free growth of high-quality monolayer graphene is preferred with a high H₂ flow, low growth temperature and thick SiO₂ coating, while bilayer or few-layer graphene are favored with lower H₂ flow, higher growth temperature and thinner SiO₂. It should be noted that we don't find any peaks of SiC (i.e., ~777, 785 and ~964 cm⁻¹) on all the metal-free-grown graphene samples, confirming that no SiC was formed in the CVD process [23].

Fig 1d shows the representative XPS survey spectra of a Si(500nm)/SiO₂ substrate before and after monolayer graphene growth. As we would have expected, only Si and O signals were detected on the pristine SiO₂/Si substrate. After graphene growth, a dominant C1s peak at ~284.5 eV verified the formation of graphite-like sp² hybridized carbon with most carbon atoms remain embedded within the honeycomb lattice. No trace of any metallic impurities was detected before and after the graphene growth. The XPS quantitative analysis shows a constant atomic ratio of Si to O (~0.5) before or after graphene growth, following the stoichiometry of bulk SiO₂ material. No apparent shoulders for the Si-C bonds (e.g., ~282 eV and ~100 eV) were found in the low energy side of C1s peak or Si2p peak, demonstrating that carbothermal reduction of SiO₂ didn't take place in the CVD process.

3.2 Growth of monolayer graphene

Fig 2a shows the photograph of a continuous monolayer graphene grown on SiO₂(500nm)/Si (inset in Fig 2a) under the optimal conditions. The uniform surface exhibits high quality of the monolayer graphene, which fully covers the SiO₂/Si substrate. The AFM image of the same sample reveals the graphene thickness of ~0.7 nm (Fig 2b), characteristic of monolayer graphene. Uniform Raman maps of the G, 2D and I_{2D}/I_G (Fig 2c-e) further confirm the homogeneous monolayer nature of graphene with a high coverage of over 95 %. Fig 2f

compares the Raman spectra taken at several randomly selected spots (marked with corresponding colors to the spectra), all showing typical features of monolayer graphene with the I_{2D}/I_G ratio of ~ 3.1 . When compared to the previously reported metal-free-grown graphene of $I_D/I_G \approx 1.5$ -2 [12-18], the much reduced ratio of $I_D/I_G = \sim 0.1$ in our samples represents a remarkable improvement and indicates the importance of controlling the CVD growth parameters to the quality of the monolayer graphene.

Fig. 2 (a) Optical microscope image of the monolayer graphene on SiO₂(500nm)/Si grown at 1065 °C for 7 h with a mixed H₂/CH₄ (120/30 sccm) flow. A scratched line was made in (a) for comparison, revealing continuous graphene fully covering the wafer. Inset shows a photograph of this graphene grown on SiO₂/Si. (b) AFM image of the monolayer graphene. The blue line near edge of the graphene indicates a thickness of ~ 0.7 nm. (c-e) Raman mapping images of (c) the G band, (d) 2D band and (e) the I_{2D}/I_G of the monolayer graphene (CCD cts, charge-coupled device counts). (f) Raman spectra from the marked spots with corresponding colored circles in (c-e).

Fig. 3 (a) Raman spectra of the graphene grown on SiO₂(500nm)/Si at 1065 °C with a mixed H₂/CH₄ (120/30 sccm) flow for different growth durations in the range of 0.5-10 hours. The spectra are scaled to produce an approximate match in intensity for 2D band. (b) Evolution of the I_D/I_G and I_{2D}/I_G of the graphene with the duration growth time.

The graphene growth on SiO₂ (500nm)/Si was also evaluated as a function of growth time. The graphene growth on SiO₂(500nm)/Si for varying growth times of 5, 7, 10, 13 and 16 h yields similar structure, as shown in Fig 3a-b. Therefore, it can be concluded that the monolayer graphene is growing on SiO₂(500nm)/Si through a surface-catalyzed process rather than a precipitation process, comparable with the case of monolayer graphene growth on Cu foil [8]. Interestingly, a similar self-limiting mechanism may also be present, which prevents nucleation of second graphene layer after the first layer is completed.

3.3 Growth of **AB stacked** bilayer graphene

Fig 4a shows that the photograph of a continuous AB-stacked bilayer graphene grown on SiO₂(90nm)/Si under the optimal conditions. It is known that Raman spectroscopy is a quick and very effective characterization method to easily distinguish the stacking orientation of bilayer graphene [24]. For example, , the asymmetric 2D peak of AB-stacked bilayer graphene can always be deconvoluted into four small peaks regardless of the used laser

excitation energies (i.e., 488, 514, 532 or 633 nm) [22, 24-31], contrary to the only one component for the monolayer graphene or the arbitrarily misoriented bilayer graphene [32].

Uniform Raman maps of the G band, 2D band and I_{2D}/I_G ratio (Fig 4b-d) demonstrates the homogeneous bilayer nature and the high coverage (over 95 %) of the graphene. Fig 4e shows Raman spectra from the randomly selected spots with corresponding colored circles, which have three characteristic peaks of graphene, i.e., 2D band at $\sim 2721\text{ cm}^{-1}$, the G band at $\sim 1586\text{ cm}^{-1}$ and D band at $\sim 1358\text{ cm}^{-1}$. The I_D/I_G ratio (~ 0.1) indicates the relatively high quality of the bilayer graphene. The I_{2D}/I_G ratio is ~ 1 , characteristic of the bilayer graphene [29, 30, 33]. Moreover, compared to monolayer graphene that has a narrow symmetric 2D peak, the asymmetric 2D band consists of four Lorentzian sub-peaks, $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$ (Fig 4f green peaks from left to right), which confirms the continuous high-quality AB-stacked bilayer graphene is successfully grown on $\text{SiO}_2(90\text{nm})/\text{Si}$ substrates.

Fig. 4 (a) Optical microscopy image of the continuous bilayer graphene on $\text{SiO}_2(90\text{nm})/\text{Si}$ at $1090\text{ }^\circ\text{C}$ for 3 h with a mixed H_2/CH_4 (120/30 sccm) flow. (b-d) Raman mappings of the G band, 2D band and I_{2D}/I_G . (e) Raman spectra from the marked spots with corresponding colored circles in (b-d). (f) Peak fitting of the 2D peak of the bilayer graphene.

It is known that the AB-stacked bilayer graphene has attracted major attention from the basic physics research community, mainly owing to its tunable band structure. Very recently, when compared to the monolayer graphene and the arbitrarily misoriented bilayer graphene, this metal-free-grown AB-stacked bilayer graphene has been found to exhibit a nontrivial charge-transfer behavior owing to the change in the electronic band structure induced by the electronic coupling between the two graphene layers, which in turn can affect the electronic coupling between graphene and the organic molecule [33].

Fig. 5 (a) Raman spectra of the graphene grown on SiO₂(90nm)/Si at 1090 °C with a mixed H₂/CH₄ (120/30 sccm) flow for different growth durations in the range of 0.5-10 hours. The spectra are scaled to produce an approximate match in intensity for 2D band. (b) Evolution of the I_D/I_G and I_{2D}/I_G of the graphene with the duration growth time.

The graphene growth was also evaluated for various growth times under the optimized conditions. In stark contrast with the case of monolayer graphene growth on SiO₂ (500nm)/Si, it is revealed that the growth time has an important influence on graphene growth on SiO₂ (90nm)/Si, as shown in Fig. 5a-b. The growth of bilayer graphene with the I_{2D}/I_G of ~1 proceeded for growth time of less than 4 h, while growth that proceeded for more than 6 h yielded few-layer graphene with the I_{2D}/I_G of 0.65-0.75. But once the duration time is over 8 h,

the concomitant amorphous carbon led to a dramatic I_D/I_G ratio increase of the few-layer graphene, suggesting a considerable quality reduction of the as-synthesized few-layer graphene. There, it is concluded that the graphene is growing on SiO_2 (90nm)/Si by another different process, rather than a surface-catalyzed mode, as we would have expected based on the SiO_2 (500nm)/Si case.

3.4 Graphene growth *models* on SiO_2 /Si with different SiO_2 layer thicknesses

It is known that the metal-catalyzed growth of graphene is realized by either carbon precipitation or surface adsorption mechanism, depending on the carbon solubility in metal catalysts used in the CVD process. For example, with low solubility of carbon, Cu can surface-catalyze CH_4 decomposition and carbon adsorption to form monolayer graphene due to a self-limit effect [8], while Ni with relatively high carbon solubility can dissolve and precipitate out carbon to form multi-layer graphene on its surface upon cooling [9]. Therefore, to obtain precise control of the quality and structure (e.g., size, layer numbers) of metal-free grown graphene on SiO_2 /Si, it is necessary to insightfully investigate the growth mechanism of the graphene. In fact, the density functional theory (DFT) calculations have suggested that SiO_2 could provide a catalytic assistance by capturing $-\text{CH}_x$ species and thus promoting C-C coupling to form sp^2 graphitic structure in growth of single-walled carbon nanotubes [34]. While a more systematic investigation is necessary, we propose a similar catalytic role of SiO_2 may be the key in controllable CVD graphene growth on SiO_2 /Si, as schematically described in Fig. 6.

Fig 6a shows the formation of graphene on SiO_2 /Si with thick SiO_2 layer facilitated by the SiO_2 -surface-catalyzed process. At large thickness, SiO_2 layer has comparable properties to bulk SiO_2 that has no carbon solubility and remains in the solid state during the entire CVD growth process due to its high melting point of $\sim 1650^\circ\text{C}$. Graphene is still growing on SiO_2 through a surface-catalyzed vapor-solid-solid (VSS) growth mode and a self-limiting effect is

present. This argument is supported by observation of continuous monolayer graphene for varying growth times from 5 to 16 h (Fig 3a-b).

Fig. 6 (a-b) Schematic illustrations of the graphene growth on SiO₂/Si with (a) thick and thin (b) SiO₂ layers.

On the other hand, SiO₂/Si substrates with thin SiO₂ layers have shown the capability of growing AB-stacked bilayer graphene and few-layer graphene as a result of growth times. This observation suggests that additional growth mode is present. It is well known that Si self-diffusion through thermally grown SiO₂ (especially for much thinner cases) at high temperatures is a fundamental physical phenomenon on a semiconductor-grade silicon wafer [35-37]. During the CVD growth of graphene at high temperatures (1060-1100 °C), it is expected that a small amount of Si atoms diffuse onto the surface of the SiO₂/Si substrate through the thin SiO₂ layer. Since Si stably absorbs active C species before a complete layer of graphene covers the surface of the SiO₂. As the C diffused in the Si atoms precipitates out upon cooling, a layer graphene can form below the graphene top layer. As a result, the growth of bilayer or few-layer graphene is preferred on SiO₂/Si with thin SiO₂ layer by a surface-adsorption combined with precipitation mode (Fig 6b), analogous to the case of AB-stacked bilayer graphene growth on binary Cu-Ni alloy foils [30, 31]. It is particularly worth mentioning that a complete bilayer graphene coverage of SiO₂/Si after 3 hours growth time is comparable to the growth rate of bilayer graphene on Cu foil [27, 29, 38].

Fig. 7 (a) Raman spectra of the graphene grown on SiO₂(500nm)/Si at 1090 °C with a mixed H₂/CH₄ (140/30 sccm) flow for different time. (b) Raman spectrum of the bilayer graphene directly grown on fused silica (Inset) at 1080 °C with a mixed H₂/CH₄ (140/30 sccm) flow. (f) Transmittance of the same bilayer graphene on fused silica.

It should be noted that graphene growth on SiO₂/Si also strongly depends on H₂ flow rate, which can even result in the alteration of graphene growth modes from monolayer to AB-stacked bilayer or few layers [25, 38, 39]. For example, with an high H₂ flow of 140 sccm under a comparable CVD process, Fig 7a shows the monolayer, bilayer and few-layer graphene grown on SiO₂(500 nm)/S through a layer-by-layer growth mode. In addition, Fig 7b shows the bilayer graphene grown on fused silica (bulk SiO₂), which has 95.2 % transmittance at wavelength of 550 nm (Fig 7c). Therefore, the multiple roles of hydrogen in the graphene growth deserve some discussion here.

Firstly, owing to a concentration of reactive H radicals produced in thermal CVD system [40], CH₄ dissociation process can be enabled by atomic hydrogen due to the abstraction reaction ($\text{CH}_4 + \text{H} \rightarrow \cdot\text{CH}_3 + \text{H}_2$) [41], thereby facilitating the growth of graphene on the surface of SiO₂/Si. Secondly, these reactive H radicals derived from appropriate H₂ flow rate (i.e., 100-160 sccm) may not considerably change the surface kinetics or block the formation of graphene on SiO₂/Si, but can determine the size, morphology, and layer number of the resulting graphene domains, similar to the case of the effect of H₂ in single-walled carbon

nanotube growth [40]. Thirdly, a moderate etching effect of the reactive H radicals can be expected on sp^2 -like carbon to form sp^3 structures and lead to the formation of the most stable graphene via the following reactions: $(\text{Graphene-C}) + \text{H} \rightarrow (\text{Graphene}) + \text{CH}_x, \text{C}_2\text{H}_y, \text{C}_3\text{H}_z$; $\text{CH}_x, \text{C}_2\text{H}_y, \text{C}_3\text{H}_z \dots + \text{H} \rightarrow \text{CH}_4 \uparrow, \text{C}_2\text{H}_6 \uparrow, \text{C}_3\text{H}_8 \uparrow \dots$. But once the H_2 flow is over 200 sccm, the enhanced etching effect of hydrogen would result in almost no graphene formation on SiO_2/Si . Finally, the amorphous carbon on graphene can be gasified and removed by the etching effect of hydrogen via the following reactions: $(\text{Graphene})-\text{CH}_n + \text{H} \rightarrow (\text{Graphene})-\text{CH}_{n+1}$ ($n=0,1,2$); $(\text{Graphene})-\text{CH}_3 + \text{H} \rightarrow (\text{Graphene}) + \text{CH}_4 \uparrow$, and consequently improving the overall quality of the resulting graphene. The effect of H_2 on graphene quality can be clearly seen in Fig 1a. With increasing H_2 flow rate from 70 sccm to 120 sccm (CH_4 flow rate fixed at 30 sccm), the intensity of the D bands decreases monotonically, mainly because of the enhanced gasification and removal of amorphous carbon by large H_2 flows. At 120 sccm, the D band becomes negligibly small. Higher H_2 flow above this optimal point leads to reappearance of the D band due to the enhanced etching effect of H_2 . This result illustrates the critical role of H_2 in controlling the quality of the graphene grown on dielectric substrates.

3.5 *Electronic properties of the metal-free-grown graphene*

The surface work function and valence band structure of the metal-catalyst-free grown monolayer and bilayer graphene on SiO_2/Si and the Cu-catalyzed bilayer graphene transferred on SiO_2/Si (for comparison) are measured using ultraviolet photoemission spectroscopy (UPS). The work function can be determined from the position of the secondary electron cutoff (SECO)-vertical lines shown in Fig 8a. **The transferred bilayer graphene has a work function (4.26 eV) and is very comparable with the previous results (~4.1-4.2 eV) [42, 43], while the directly-grown monolayer graphene and bilayer graphene has a work function of 4.46 eV and 4.5 eV respectively.** The valence band spectra of the three samples are shown in

Fig 8b. The π and σ band can be resolved by using 40.81 eV photons (dashed lines) [44]. Comparing to the transferred graphene, the position of the π band for metal-free-grown bilayer graphene shifts away from the Fermi level by -0.26 eV. Both the π -band and SECO is shifted by a similar amount in the metal-free-grown monolayer and bilayer graphene, which indicates that the increase of the work function is caused by a downshift in the Fermi-level. The observed p-type doping is likely to be caused by the enhanced coupling between the metal-free-grown graphene and the SiO_2 surface induced by high graphene growth temperature in the CVD process.

Fig. 8 UPS spectra for the as-grown monolayer (blue line) and bilayer graphene (green line) grown on SiO_2/Si and the Cu-catalyst-grown bilayer graphene transferred on SiO_2/Si (red line) for comparison. Solid and dashed lines represent spectra collected with 21.22 eV and 40.81 eV photons respectively. The energy is referenced to the Fermi level E_f . (c-d) I_{ds} - V_{bg} transfer characteristics at 0.4 V_{ds} for (c) monolayer and (d) bilayer graphene.

The graphene field-effect transistors (GFET) of the directly-grown monolayer and bilayer graphene on SiO₂/Si back gate were fabricated by standard two-step photolithography processes. The graphene was first patterned to a stripe (20 μm × 20 μm) by O₂ plasma etching. Then, the source-drain electrodes of Ti (10 nm)/Au(60 nm) were deposited by electron beam evaporation. The electrical characteristics were measured in a vacuum (~10⁻⁶ torr) probe station at room temperature. Fig 8c-d shows the source-drain current (I_{ds}) versus gate voltage (V_{bg}) under different source-drain voltage (V_{ds}) for monolayer and bilayer graphene FET, respectively. It is not surprising that the ability of the gate voltage tuning the charge in the graphene is weak due to the large thickness of the gate dielectric (500 nm SiO₂) and the enhanced coupling between the metal-free-grown graphene and the SiO₂ surface induced by high graphene growth temperature in the CVD process. Similar phenomena are also observed for the transferred graphene when high-temperature thermal annealing (i.e., over 350 °C) is applied during the transfer process [45, 46]. The mobility can still be calculated by the gate effect by extracting conductivity of I_{ds} - V_{bg} curves at $V_{ds}=0.4$ V, that is by formula $\mu=(L/WCV_{ds})(dI/dV_{bg})$, where $L=20$ μm and $W=20$ μm are the channel length and width of FET, respectively, $C=6.902\times10^{-10}$ F/cm² is the gate dielectric capacitance. The mobilities of the monolayer and the bilayer graphene FET are 80.1 and 63.4 cm²/Vs, respectively. These data suggest that the metal-free-grown graphene on SiO₂/Si is of reasonable quality, when compared to that of grown on Cu, Ni and other metals. Further work (e.g., by doing or functionalizing graphene) is still needed to carry on to improve the electronic properties of the directly-grown graphene on SiO₂/Si.

4. Conclusions

In summary, high-quality monolayer and AB-stacked bilayer and few-layer graphene have been successfully grown on SiO₂/Si in absence of metal catalysts. A crucial catalytic role of SiO₂ in graphene growth on SiO₂/Si substrates has been confirmed with self-limiting

mechanism similar to that observed on Cu substrates. Reducing the SiO₂ layer thickness promotes atomic Si diffusion through the SiO₂ to the substrate surface, resulting in bilayer to few layer graphene growth as C diffused in atomic Si precipitates out during cooling. This interesting SiO₂ layer thickness effect allows graphene growth with controllable layer number in CVD process. In addition, while the layer-by-layer growth mode is suppressed at lower H₂ flow rates, it prevails at high ones, allowing controlling graphene layer numbers using CVD growth time. The achieved understanding of CVD parameter in combination with the catalytic role of SiO₂ layer thickness is important and paves a way for the controllable synthesis of monolayer and AB-stacked bilayer or few layer graphene directly on technologically important SiO₂/Si substrates.

Acknowledgements

The authors acknowledge support in part by ARO contract No. ARO-W911NF-12-1-0412, and NSF contracts Nos. NSF-DMR-1105986 NSF-DMR-1337737, and NSF-DMR-1508494. WLC acknowledges support from US National Science Foundation, grant DMR-1351716.

REFERENCES

- [1] Geim AK. Graphene: Status and Prospects. *Science*. 2009;324(5934):1530-4.
- [2] Rogers GW, Liu JZ. Graphene Actuators: Quantum-Mechanical and Electrostatic Double-Layer Effects. *J Am Chem Soc*. 2011;133(28):10858-63.
- [3] Wu ZS, Yang SB, Sun Y, Parvez K, Feng XL, Mullen K. 3D Nitrogen-Doped Graphene Aerogel-Supported Fe₃O₄ Nanoparticles as Efficient Electrocatalysts for the Oxygen Reduction Reaction. *J Am Chem Soc*. 2012;134(22):9082-5.
- [4] Cai JM, Ruffieux P, Jaafar R, Bierl M, Braun T, Blankenburg S, et al. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature*. 2010;466(7305):470-3.

- [5] Berger C, Song ZM, Li XB, Wu XS, Brown N, Naud C, et al. Electronic confinement and coherence in patterned epitaxial graphene. *Science*. 2006;312(5777):1191-6.
- [6] Choucair M, Thordarson P, Stride JA. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nat Nanotechnol*. 2009;4(1):30-3.
- [7] Kosynkin DV, Higginbotham AL, Sinitskii A, Lomeda JR, Dimiev A, Price BK, et al. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature*. 2009;458(7240):872-7.
- [8] Li XS, Cai WW, An JH, Kim S, Nah J, Yang DX, et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science*. 2009;324(5932):1312-4.
- [9] Kim KS, Zhao Y, Jang H, Lee SY, Kim JM, Kim KS, et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*. 2009;457(7230):706-10.
- [10] Li XS, Zhu YW, Cai WW, Borysiak M, Han BY, Chen D, et al. Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes. *Nano Lett*. 2009;9(12):4359-63.
- [11] Lee Y, Bae S, Jang H, Jang S, Zhu SE, Sim SH, et al. Wafer-Scale Synthesis and Transfer of Graphene Films. *Nano Lett*. 2010;10(2):490-3.
- [12] Sun J, Lindvall N, Cole MT, Wang T, Booth TJ, Boggild P, et al. Controllable chemical vapor deposition of large area uniform nanocrystalline graphene directly on silicon dioxide. *J Appl Phys*. 2012;111(4).
- [13] Bi H, Sun SR, Huang FQ, Xie XM, Jiang MH. Direct growth of few-layer graphene films on SiO₂ substrates and their photovoltaic applications. *J Mater Chem*. 2012;22(2):411-6.
- [14] Hong G, Wu QH, Ren JG, Lee ST. Mechanism of non-metal catalytic growth of graphene on silicon. *Appl Phys Lett*. 2012;100(23):231604.
- [15] Zhang L, Shi Z, Wang Y, Yang R, Shi D, Zhang G. Catalyst-free growth of nanographene films on various substrates. *Nano Research*. 2011;4(3):315-21.

- [16] Wei DP, Xu XF. Laser direct growth of graphene on silicon substrate. *Appl Phys Lett*. 2012;100(2):023110.
- [17] Tian SB, Li L, Sun WN, Xia XX, Han D, Li JJ, et al. Robust adhesion of flower-like few-layer graphene nanoclusters. *Sci Rep-Uk*. 2012;2:511.
- [18] Medina H, Lin YC, Jin CH, Lu CC, Yeh CH, Huang KP, et al. Metal-Free Growth of Nanographene on Silicon Oxides for Transparent Conducting Applications. *Adv Funct Mater*. 2012;22(10):2123-8.
- [19] Chen JY, Wen YG, Guo YL, Wu B, Huang LP, Xue YZ, et al. Oxygen-Aided Synthesis of Polycrystalline Graphene on Silicon Dioxide Substrates. *J Am Chem Soc*. 2011;133(44):17548-51.
- [20] Dresselhaus MS, Dresselhaus G, Jorio A, Souza AG, Saito R. Raman spectroscopy on isolated single wall carbon nanotubes. *Carbon*. 2002;40(12):2043-61.
- [21] Gupta A, Chen G, Joshi P, Tadigadapa S, Eklund PC. Raman scattering from high-frequency phonons in supported n-graphene layer films. *Nano Lett*. 2006;6(12):2667-73.
- [22] Ferrari AC, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, et al. Raman spectrum of graphene and graphene layers. *Phys Rev Lett*. 2006;97(18):187401.
- [23] Harima H. Raman scattering characterization on SiC. *Microelectron Eng*. 2006;83(1):126-9.
- [24] Fang W, Hsu AL, Caudillo R, Song Y, Birdwell AG, Zakar E, et al. Rapid Identification of Stacking Orientation in Isotopically Labeled Chemical-Vapor Grown Bilayer Graphene by Raman Spectroscopy. *Nano Lett*. 2013;13(4):1541-8.
- [25] Liu QF, Gong YP, Wilt JS, Sakidja R, Judy W. Synchronous Growth of AB-Stacked Bilayer Graphene on Cu by Simply Controlling Hydrogen Pressure in CVD Process. *Carbon*. 2015;93:199-206.
- [26] Peng ZW, Yan Z, Sun ZZ, Tour JM. Direct Growth of Bilayer Graphene on SiO₂ Substrates by Carbon Diffusion through Nickel. *ACS Nano*. 2011;5(10):8241-7.

- [27] Luo ZQ, Yu T, Shang JZ, Wang YY, Lim S, Liu L, et al. Large-Scale Synthesis of Bilayer Graphene in Strongly Coupled Stacking Order. *Adv Funct Mater.* 2011;21(5):911-7.
- [28] Yan Z, Peng ZW, Sun ZZ, Yao J, Zhu Y, Liu Z, et al. Growth of Bilayer Graphene on Insulating Substrates. *ACS Nano.* 2011;5(10):8187-92.
- [29] Yan K, Peng HL, Zhou Y, Li H, Liu ZF. Formation of Bilayer Bernal Graphene: Layer-by-Layer Epitaxy via Chemical Vapor Deposition. *Nano Lett.* 2011;11(3):1106-10.
- [30] Liu W, Kraemer S, Sarkar D, Li H, Ajayan PM, Banerjeet K. Controllable and Rapid Synthesis of High-Quality and Large-Area Bernal Stacked Bilayer Graphene Using Chemical Vapor Deposition. *Chem Mat.* 2014;26(2):907-15.
- [31] Wu YP, Chou H, Ji HX, Wu QZ, Chen SS, Jiang W, et al. Growth Mechanism and Controlled Synthesis of AB-Stacked Bilayer Graphene on Cu-Ni Alloy Foils. *ACS Nano.* 2012;6(9):7731-8.
- [32] Poncharal P, Ayari A, Michel T, Sauvajol JL. Raman spectra of misoriented bilayer graphene. *Phys Rev B.* 2008;78(11):113407.
- [33] Liu W, Li H, Xu C, Khatami Y, Banerjee K. Synthesis of high-quality monolayer and bilayer graphene on copper using chemical vapor deposition. *Carbon.* 2011;49(13):4122-30.
- [34] Liu BL, Tang DM, Sun CH, Liu C, Ren WC, Li F, et al. Importance of Oxygen in the Metal-Free Catalytic Growth of Single-Walled Carbon Nanotubes from SiO(x) by a Vapor-Solid-Solid Mechanism. *J Am Chem Soc.* 2011;133(2):197-9.
- [35] Takahashi T, Fukatsu S, Itoh KM, Uematsu M, Fujiwara A, Kageshima H, et al. Self-diffusion of Si in thermally grown SiO₂ under equilibrium conditions. *J Appl Phys.* 2003;93(6):3674-6.
- [36] Tsoukalas D, Tsamis C, Normand P. Diffusivity measurements of silicon in silicon dioxide layers using isotopically pure material. *J Appl Phys.* 2001;89(12):7809-13.
- [37] Kageshima H, Shiraishi K. First-principles study of oxide growth on Si(100) surfaces and at SiO₂/Si(100) interfaces. *Phys Rev Lett.* 1998;81(26):5936-9.

- [38] Liu LX, Zhou HL, Cheng R, Yu WJ, Liu Y, Chen Y, et al. High-Yield Chemical Vapor Deposition Growth of High-Quality Large-Area AB-Stacked Bilayer Graphene. *ACS Nano*. 2012;6(9):8241-9.
- [39] Zhang XY, Wang L, Xin J, Yakobson BI, Ding F. Role of Hydrogen in Graphene Chemical Vapor Deposition Growth on a Copper Surface. *J Am Chem Soc*. 2014;136(8):3040-7.
- [40] Liu QF, Ren WC, Chen ZG, Wang DW, Liu BL, Yu B, et al. Diameter-selective growth of single-walled carbon nanotubes with high quality by floating catalyst method. *ACS Nano*. 2008;2(8):1722-8.
- [41] Meyyappan M, Delzeit L, Cassell A, Hash D. Carbon nanotube growth by PECVD: a review. *Plasma Sources Science & Technology*. 2003;12(2):205-16.
- [42] Kwon KC, Choi KS, Kim SY. Increased Work Function in Few-Layer Graphene Sheets via Metal Chloride Doping. *Adv Funct Mater*. 2012;22(22):4724-31.
- [43] Wu QH, Hong G, Ng TW, Lee ST. Substrate effect on the electronic structures of CuPc/graphene interfaces. *Appl Phys Lett*. 2012;100(16):161603.
- [44] Stroscov VN, Charrier A, Themlin JM, Rohlfing M, Claessen R, Barrett N, et al. Photoemission from graphite: Intrinsic and self-energy effects. *Phys Rev B*. 2001;64(7):075105.
- [45] Nourbakhsh A, Cantoro M, Klekachev A, Clemente F, Soree B, van der Veen MH, et al. Tuning the Fermi Level of SiO₂-Supported Single-Layer Graphene by Thermal Annealing. *J Phys Chem C*. 2010;114(15):6894-900.
- [46] Cheng ZG, Zhou QY, Wang CX, Li QA, Wang C, Fang Y. Toward Intrinsic Graphene Surfaces: A Systematic Study on Thermal Annealing and Wet-Chemical Treatment of SiO₂-Supported Graphene Devices. *Nano Lett*. 2011;11(2):767-71.