

Noncatalytic chemical vapor deposition of graphene on high-temperature substrates for transparent electrodes

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A noncatalytic chemical vapor deposition mechanism is proposed, where high precursor concentration, long deposition time, high temperature, and flat substrate are needed to grow large-area nanocrystalline graphene using hydrocarbon pyrolysis. The graphene is scalable, uniform, and with controlled thickness. It can be deposited on virtually any nonmetallic substrate that withstands ~ 1000 °C. For typical examples, graphene grown directly on quartz and sapphire shows transmittance and conductivity similar to exfoliated or metal-catalyzed graphene, as evidenced by transmission spectroscopy and transport measurements. Raman spectroscopy confirms the sp^2 -C structure. The model and results demonstrate a promising transfer-free technique for transparent electrode production.

Graphene, a monolayer of sp^2 carbon atoms, has received much attention. The use of graphene in transparent electronics is one of its most promising applications.¹ Apart from its high transparency/conductivity, the flexibility and ease of integration on a variety of substrates are obvious advantages. 30-inch graphene has been demonstrated by virtue of the recent advances in chemical vapor deposition (CVD),² which is compatible with the existing semiconductor technology.³ Nevertheless, the necessity of etching the metal catalyst and transfer of graphene to foreign substrates hampers wide industrialization. Thus, efforts are put into the metal-free growth of graphene on materials including SiO_2 ,⁴⁻⁶ Al_2O_3 ,⁷ MgO ,⁸ etc. To date, however, the graphitization process on dielectrics is poorly understood while the experiments are largely experience based. Recently, we have shown that large-area uniform graphene can be grown on virtually any high-temperature substrates, on Si_3N_4 or HfO_2 , for instance.⁹ In this letter, we provide a broader and deeper insight, discussing in detail the growth mechanism of graphene directly on insulators. As an example, we show our results on graphene on quartz and sapphire, hinting at the future prospects of the transfer-free graphene for transparent electrodes.

Bulk graphite is usually made at >3000 °C and catalysis is needed to lower the temperature.¹⁰ However, nanoscale graphene flakes form without any catalysts at merely ~ 1000 °C. For example, carbon black which is produced massively by natural gas pyrolysis¹¹⁻¹⁴ is nothing else but chaotically connected graphene flakes.¹¹ Although widely used in industry, this process has so far been overlooked for making large-area graphene. Here, we show that macroscopically amorphous carbon black can be turned into textured graphene thin films when

the carbon precursor concentration and growth temperature are high, also requiring a relatively long deposition time and flat substrate.

Fig. 1(a) illustrates the CVD reactor used in this work. The middle region is heated to 1000 °C while the left and right sides are <600 °C. There is no material deposition in the right zone because of the reduced CH_4 decomposition efficiency at lower temperature. Carbon black is seen on the left, as an evidence of the CH_4 dissociation in the middle zone. The easiest way to distinguish graphene from carbon black is to observe their optical appearances. The as-grown graphene is smooth and, on any high-temperature substrate, keeps its metallic luster (see Fig. 1(b)) for hundreds of layers,⁹ whereas carbon

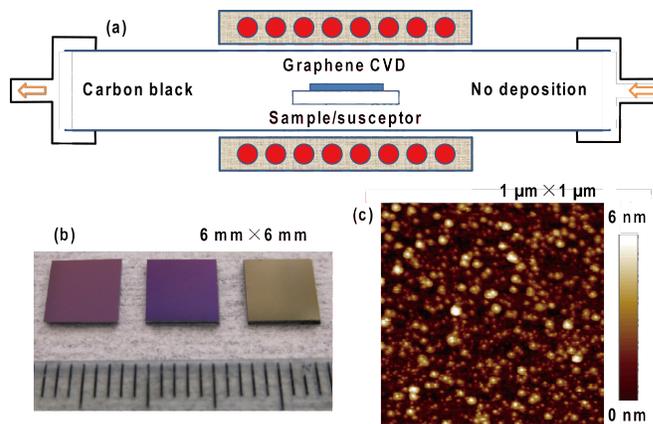


FIG. 1. (Color online) (a) Schematic of the hot-wall CVD system used in this study, indicating zones where graphene and carbon black are deposited. The arrows indicate the direction of gas flow. (b) Photo of bare 300 nm SiO_2/Si (left) and with coated nominal monolayer graphene (middle) and ~ 70 nm graphite (right). (c) Atomic force microscopy micrograph of the middle sample in (b), where $r_a \approx 1$ nm.

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black is dull black even for thinner films. Fig. 1(b) shows the photo of (right to left) ~ 70 nm thick graphite, monolayer graphene, and the bare substrate (300 nm SiO_2/Si), respectively. The growth recipe is similar to our previous work, where the thickness is controllable from nominally submonolayer to thick graphite.⁹ Transmission electron microscopy reveals that the middle sample in Fig. 1(b) is composed of primarily ~ 10 nm large monolayer graphene crystallites.¹⁵ The high density of grain boundaries is fundamental which results in strong scattering of charge carriers and makes such graphene unsuitable for transistors. Nonetheless, this does not reduce its value for applications where transparency of electrodes (e.g. solar cells/displays) or their thickness (e.g. molecular electronics) are more important than the mobility. Indeed, the optical similarity between this graphene and exfoliated- or Cu-catalyzed monolayer graphene¹⁶ is evidenced by ellipsometry measurements.¹⁵ Fig. 1(c) is an atomic force microscopy image¹⁵ of the middle sample in Fig. 1(b). The arithmetic average roughness r_a is ~ 1 nm, which is reasonable for nanocrystalline graphene resting on thermally grown SiO_2 (r_a is ~ 0.2 nm).

Fig. 2 shows the transmission spectra of nominal monolayer graphene deposited on quartz and sapphire.¹⁵ The transmittance of graphene is generally independent of the light wavelength,¹⁷ except a dip at ~ 270 nm, which is due to the exciton-shifted van Hove singularity in the graphene density of states.¹⁸ After the coating, the transmittances of quartz and sapphire are reduced by ~ 2 -3%, values similar to exfoliated graphene.¹⁷ The inset of Fig. 2(a) shows the Fourier transform infrared spectroscopy (FTIR) measurements on the same samples. The spectra have no C-related peaks after CVD, implying atomic-scale thickness. The curves before and after graphene growth are very similar (no additional features in 3000 - 3700 cm^{-1} range),^{19,20} suggesting the lack of $-\text{OH}$ groups. This offers an advantage over the wet-transferred graphene, where H_2O is likely to be trapped at the interfaces. The Raman spectra of the graphene on quartz and sapphire are displayed in the inset of Fig. 2(b). The well-defined Raman peaks differentiate our thin films from amorphous C (a -C).²¹ In fact, atomically thin a -C films have never been realized by CVD.²² The G band centered at 1600 cm^{-1} and the 2D band at 2695 cm^{-1} are well resolved, which are signatures of sp^2 graphitic materials. D peaks at 1353 cm^{-1} are also seen. This Raman mode is forbidden in perfect graphitic structure and only becomes active in the presence of disorder.²³ In our case, the laser spot is ~ 10 μm and covers numerous grain boundaries of the nanocrystalline graphene, which naturally results in large D signals. Consequently, high-order G+D bands at 2946 cm^{-1} are visible. The ratio of D- and G peak heights²⁴ allows estimation of the average distance between defects ~ 7 -9 nm, consistent with the grain size ~ 10 nm of our thin films.¹⁵ Hall-bar devices are fabricated from these samples by photolithography.¹⁵ Room-temperature four-terminal electrical measurements indicate the sheet

resistance R_s of 2.9 and 13 $\text{k}\Omega/\square$ for the quartz- and sapphire-supported graphene, respectively. Again, R_s is comparable to that of standard graphene.¹⁸

Thermal dissociation of methane is described as $\text{CH}_4 = \text{C} + 2\text{H}_2$ ($\Delta H^\circ = 75.6$ kJ/mol). Although CH_4 is one of the most stable organic molecules due to a strong C–H bond of 440 kJ/mol,²⁵ the reaction readily occurs at ≥ 300 $^\circ\text{C}$ and becomes nearly complete at ≥ 1300 $^\circ\text{C}$.¹⁴ When a metal catalyst is present,^{2,3,16} both the hydrocarbon decomposition and graphene formation are boosted. Consequently, graphene grows rapidly at a very low hydrocarbon partial pressure.¹⁶ Without using metals, which we refer to as “nong catalytic graphene CVD”,^{10,26} the deposition requires a much higher methane concentration (~ 200 vs. ~ 0.01 mbar) and longer growth time (30 vs. 5 min).^{9,16}

The graphene thin-film formation on nonmetallic substrates appears to be different from the mechanism common to e.g. metallic thin films. Indeed, graphene flakes are readily formed in the gas mixture surrounding a hot substrate. The flakes landing on the substrate can have various fates depending on their sizes. Large enough flakes would stick and stay at the surface, reminiscent of the critical-size nuclei in the common thin-film nucleation theory.²⁷ The smaller flakes would not adhere

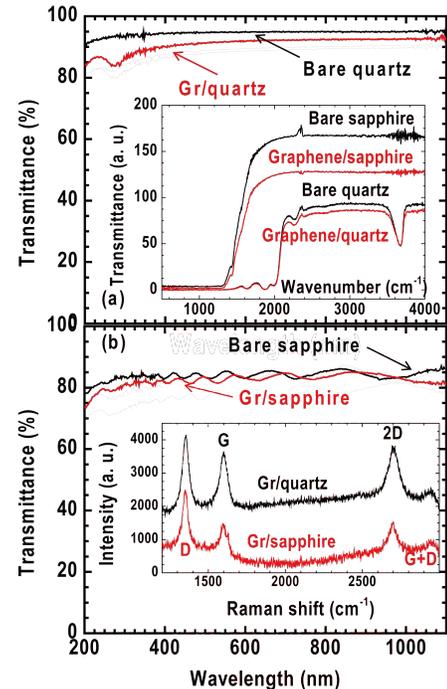


FIG. 2. (Color online) Transmittance spectra of the nong catalytic CVD graphene on (a) quartz and (b) sapphire. The curves in (b) have superimposed interference fringes from the sapphire substrates. Inserts: (a) FTIR spectra of the quartz and sapphire before and after the nong catalytic graphene growth; (b) Raman spectra (514 nm, 3 mW) of the samples. “Gr” denotes graphene.

to the substrate strongly enough to sustain high-energy thermal vibrations and would leave the substrate, unless they happened to be near the stable flakes (“nuclei”) that are already present at the surface and make bonds to them. Stacking of the flakes on top of each other is improbable because the out-of-plane bonding energy between the flakes is lower than their adhesion to the substrate, as in the case of SiO₂,^{28,29} impeding formation of the second layer. Reorientation and alignment of the nm-sized flakes requires temperatures >2000 °C,³⁰ and is unlikely to occur in our case, resulting in disordered thin films.

In this picture, the usual growth mechanism, when single atoms have some time to diffuse along the surface and adjoin the stable nuclei, is somehow suppressed, much likely because of the high temperature and the weak adhesion of single atoms to substrate. Next-layers growth, although initially broken short, is still possible after the first graphene layer is formed. Due to a lower graphene-to-graphene cohesion energy (compared with the adhesion to SiO₂),^{28,29} larger flakes would now be needed to make stable islands and initiate the growth of the second layer. In principle, the formation of the second- and subsequent layers should then take longer time compared to the first one. However, this difficulty might be compensated for by many defects and dangling bonds at the surface from a nonideality of the first-layer coverage,³⁰ resulting in more sites for graphene flake adsorption.

Importantly, all this means that the graphene thin film will grow much quicker with nanoflakes forming already in the gas first, making high precursor pressure and relatively long deposition time crucial. A hot and flat substrate helps preventing large porous lumps of carbon black to form,^{11–14} as there are no sites or bonding strength to attach misplaced flakes with “wrong” orientation.¹⁵ A similar example can be found in liquid phase deposition, where flat substrates help sol particles to form thin films as opposed to the otherwise favorable clumpy precipitates.^{19,20} The discussion above can be generalized to explain graphene growth on any non-metallic substrate that withstands ~1000 °C by CVD using hydrocarbons, not limited to CH₄. Obviously, the substrate materials and their preparation play an important role in the growth kinetics. On specially annealed SiO₂ where there are possibly less dangling bonds, the growth takes much longer time, but also leads to higher quality of the graphene.³¹

In summary, we have proposed a noncatalytic graphitization mechanism in graphene CVD directly on arbitrary high-temperature insulating substrates. Four experimental conditions—high carbon precursor pressure, long growth time, high temperature, and flat substrate—are needed to modify carbon black deposition into self-assembled nanocrystalline graphene thin film. The as-produced graphene is uniform, scalable, and has properties similar to standard graphene, as confirmed by transmission, FTIR and Raman spectra, as well as transport measurements. This work should stimulate further

studies on graphene grown in metal-free processes which are important for applications involving transparent electrodes.

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