Chemical Vapor Deposition of Nanocrystalline Graphene Directly on Arbitrary High-temperature Insulating Substrates

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Abstract—**Large area uniform nanocrystalline graphene is grown by chemical vapor deposition on arbitrary insulating substrates that can survive ~1000 °C. The as-synthesized graphene is nanocrystalline with a domain size in the order of ~10 nm. The material possesses a transparency and conductivity similar to standard graphene fabricated by exfoliation or catalysis. A noncatalytic mechanism is proposed to explain the experimental phenomena. The developed technique is scalable and reproducible, compatible with the existing semiconductor technology, and thus can be very useful in nanoelectronic applications such as transparent electronics, nanoelectromechanical systems, as well as molecular electronics.**

***Keywords*—Graphene, chemical vapor deposition, insulator, nanoelectronics**

I. INTRODUCTION

Graphene is a novel nanoelectronic material which has recently been intensively studied. The intrinsic mobility is extremely high. Together with its atomic-scale thickness, this material has been suggested as a potential candidate for post-silicon electronics. Nevertheless, it does not have a bandgap, leading to a small on-off ratio in transistors. Also, the experimentally demonstrated mobility falls far below the theoretically predicted value. Thus, graphene based computer processors are unlikely to be realized very soon.

This notwithstanding, there are several fields in nanoelectronics where graphene can play a key role in future: transparent electronics, nanoelectromechanical systems (NEMS), molecular electronics, etc. With the recent advances in chemical vapor deposition (CVD), large area graphene can be fabricated massively [1]. This technology is cost-effective and scalable. It is the most promising route towards industrial applications. However, metal catalysts used in the CVD need to be etched away for the transfer of graphene onto foreign insulating substrates. There is an urgent need to develop a catalyst-free method to directly synthesize graphene on dielectrics.

For some time, the noncatalytic graphene CVD in large area has been considered impossible, or at least very difficult. But recently, for the first time, we have demonstrated the uniform graphene on insulators such as Si_3N_4 and HfO_2 by metal-free CVD [2]. We also predict that this type of graphene can be grown on virtually any substrate that withstands ~1000 °C [2]. A few other groups also achieved similar results [3]. Nevertheless, the mechanism is not understood and the experiments are largely experience based. In this paper, we propose a noncatalytic mechanism of graphene growth based on the pyrolysis of hydrocarbon. More detailed description will be published elsewhere [4]. We also give examples of such a graphene on SiO_2, Al_2O_3 and GaN substrates and discuss its optical, electrical, and mechanical properties.

II. GROWTH MODEL

Herein, we propose a model to explain the noncatalytic

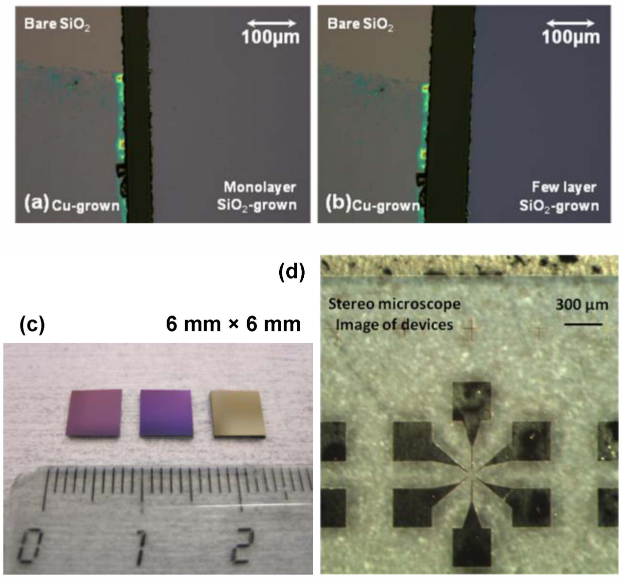

Fig. 1. (a) and (b) Color comparison of the Cu-catalyzed graphene (transferred to 300 nm SiO_2/Si) and the graphene grown directly on the same type of substrate. (c) Photo of (from left to right) bare SiO_2/Si substrate and SiO_2/Si with deposited monolayer graphene and thick graphite (~70 nm). (d) Stereo microscope image of Hall-bar devices fabricated in the multilayer graphene deposited on GaN/sapphire wafer.

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graphene growth. It is known that hydrocarbons decompose without the need of any catalyst. For example, in industry, methane pyrolysis is widely used to synthesize carbon black in large quantities [5]. This process is important, because it is a simple method for C and H_2 production without generating any CO_2. However, it has so far been over looked in terms of graphene growth. Note that carbon black is randomly stacked nanoscale graphene flakes [6]. Therefore, if a substrate is flat and high-temperature stable, the carbon black can be turned into textured graphene thin films. Due to the fact that metal catalysts are absent, high carbon precursor concentration and long deposition time are also needed to form graphene thin films.

After the hydrocarbon is decomposed, the carbon atoms readily form airborne nanographene flakes. Larger flakes have enough adhesion energy to the substrate, whereas smaller ones will have to leave the substrate at ~1000 ^{o}C. The growth is not self-limited, which means that the thickness of the graphene is controllable from submonolayer to thick graphite. In the hot-wall quartz-tube CVD reactor used in this work, the middle region is heated to ~1000 ^{o}C while the two ends (gas inlet and outlet) of the quartz reactor are at temperatures less than 600 ^{o}C. No carbon deposition is found at the gas inlet part of the quartz tube due to the absence of effective pyrolysis of methane. In the middle zone, graphene growth occurs on various substrates such as SiO_2, Al_2O_3, MgO, SiC, Si, etc. Our detailed growth conditions are described elsewhere [2, 4]. At the gas outlet part of the quartz tube, carbon black deposition occurs. Figs. 1(a) and (b) show optical images of nominal monolayer and few layer graphene grown directly on 300 nm SiO_2/Si, where the left section in each picture is a transferred Cu-grown graphene on the same type of substrates for comparision. It is known that Cu-catalyzed graphene is a monolayer (within certain parameter windows) because of the self-limiting growth mechanism [1, 7]. Based on the color comparison [8], the SiO_2-grown graphene shown in in Fig. 1(a) is much likely also a single layer. Fig. 1(c) shows the photo of (left to right) bare 300 nm SiO_2/Si substrate, monolayer graphene and thick graphite (~70 nm) on SiO_2/Si, respectively. In this figure, the films keep their metallic luster even for hundreds of layers. If, however, the temperature is not high enough, or the wafer is rough, carbon black films with a dull black color are then produced, which can hardly be useful in electronics. Fig. 1(d) demonstrates the photo of a finished Hall-bar device fabricated on GaN(0001)/sapphire substrate at 950 ^{o}C. For the first time, large-area graphitic thin films are grown directly on GaN for potential applications in optoelectronics.

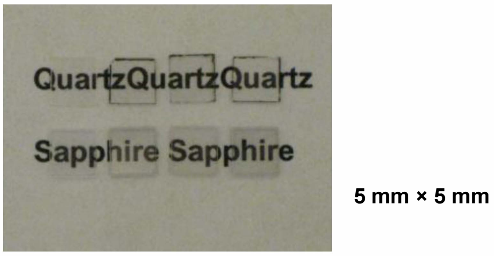

Fig. 2. Photo of 5 mm × 5 mm graphene samples on quartz and sapphire. In each row, the left is the bare substrate. Three nominal monolayer graphene samples are placed in the right showing high process reproducibility. The text behind is clearly visible due to the high transparency.

We also grow graphene on double-side polished 5 mm × 5 mm quartz and sapphire substrates. Fig. 2 shows a photo of the samples after the CVD. In each row, three nominal monolayer graphene samples grown in different runs are placed to the right. Graphene which is unintentionally deposited at the bottoms of samples has been removed by oxygen plasma etching. These samples are very similar, indicating high reproducibility in the CVD process. The text on the paper below the samples is clearly seen, showing their high transparency. The left-most sample is the bare quartz (sapphire) for comparison. The edges of the quartz samples are rough after dicing, resulting in carbon black deposits after the CVD (notice the black edge of the quartz samples in Fig. 2). In contrast, the edges of sapphire substrates have been polished after cutting, and therefore carbon black is absent. This fact suggests the importance of substrate flatness in the deposition of nanocrystalline graphene. At rough places, there are numerous kinks, pits and steps, etc. Smaller or misaligned (inclined or vertical) graphene flakes are easier to be adsorbed onto these sites forming carbon black. These defects on the substrate would not be important if the thin film were grown from individual carbon atoms. Therefore, it provides evidence that the major mechanism of the deposition is indeed based on graphene nanoflakes. In our recipe, we completely remove the carbon precursor gas immediately after the graphene growth preventing flake formation during cooling down. This growth mechanism can be used to explain nonocrystalline graphene formation in common CVD systems with relatively large quantities of precursor material. Nevertheless, in molecular beam epitaxy [9, 10] with typically much smaller carbon-atom fluxes and much longer deposition times, the growth mode is most likely based on single C atoms. Further study is needed to understand the mechanism thoroughly in these cases.

Here, due to the above-mentioned mechanism, the graphene is fundamentally nanocrystalline. Therefore, one can only speak about average number of layers. The exact number of layers is only meaningful locally. For example, the middle sample in Fig. 1(c) primarily consists of monolayer flakes; but that does not exclude the coexistence of multilayer flakes at some other spots. Besides, flakes do not have enough mobility to freely diffuse along the surface to rearrange themselves at 1000 ^{o}C, and thus at the grain boundaries some overlap may happen, resulting in a slightly rougher film (roughness ~1 nm) compared with single-crystalline graphene (resting on thermally oxidized Si).

III. OPTICAL AND ELCTRICAL PROPERTIES

After the graphene coating, the transmittances of quartz and sapphire are reduced by only 2-3% measured by transmission spectroscopy [4], which is similar to the case of exfoliated or metal-catalyzed monolayer graphene. Both on quartz and sapphire, G and 2D peaks are clearly detected in the Raman spectra [4], confirming that the deposited thin films have *sp*^{2} hybridized graphitic structures. The laser used in the Raman measurement has a beam spot of ~10 µm in size, which covers numerous crystallites in the graphene thin film. These grain boundaries naturally lead to a relatively high D peak [4] (D stands for disorder).

Hall-bar devices are fabricated by photolithography on these graphene samples on quartz, sapphire, GaN and SiO_2/Si. At room temperature, the sheet resistance R_s of the quartz and sapphire based graphene is 2.9 and 13 kΩ/□, respectively. These values are again comparable to that of intrinsic graphene produced by other means. Interestingly, on GaN, we have found that the deposited graphene has quasi-ohmic contacts to the underlying GaN, which is very promising towards solving the "current crowding" problem in GaN based lasers, etc. Also, the GaN is strongly doped after the CVD. We ascribe the observed effects to the high-temperature process during the CVD. Currently, we are investigating this and the results will be published elsewhere. For the nanocrystalline graphene grown on 300 nm SiO_2/Si, it is possible to apply gate voltages using the doped silicon substrate as a back gate. By analyzing the field effect at room temperature, we obtain a hole mobility of ~40 cm^2/Vs, which is further confirmed by Hall-effect measurements.

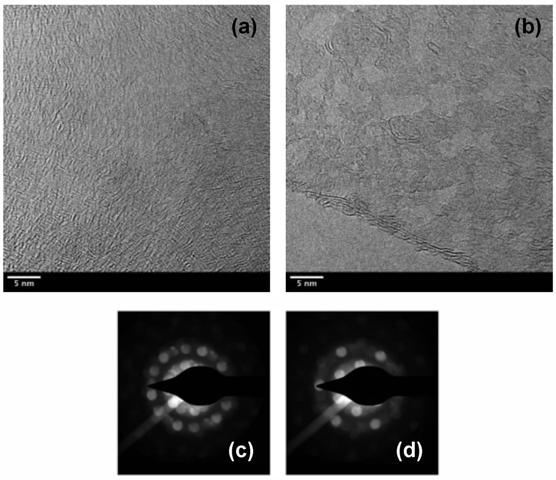

Fig. 3. (a) and (b) High-resolution TEM images of the SiO_2/Si-grown graphene transferred to Cu grids. After very long time observation, holes are burnt in the thin film, as are visible in (b). Scale bar: 5 nm. (c) and (d) Converged beam electron diffraction pattern obtained from the graphene thin films. (c) Mixed signals from two or more domains. (d) Typical monolayer graphene diffraction pattern is clearly observed reproducibly everywhere in the membrane, as long as the beam spot is ~10 nm or smaller..

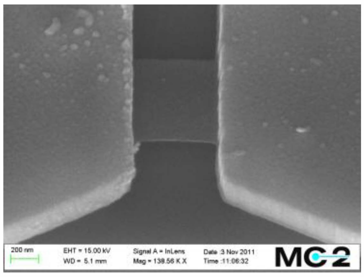

Fig. 4. SEM image of a typical suspended-channel graphene device fabricated from the SiO_2/Si-grown graphene. Scale bar: 200 nm.

IV. SUSPENDED GRAPHENE

Figs. 3(a) and (b) show two high-resolution transmission electron microscopy (TEM) images of the graphene (transferred to Cu grids with holey carbon films) grown directly on SiO_2/Si. In Fig. 3(a), the graphene membrane is rather uniform. Converged beam electron diffraction pattern clearly shows a monolayer crystal lattice feature (Fig. 3(d)). As far as we know, the hexagonal diffraction pattern of nanocrystalline graphene has not been reported before. Such a pattern is a direct evidence of the graphene nature of this type of thin films. Fig. 3(c) is a diffraction pattern obtained when the focused beam spot is somewhat larger than ~10 nm. Signals from two or multiple randomly oriented domains destroy the hexagonal pattern. By varying the beam size, we can thereby obtain an indirect estimate of the domain size. Although the domains are only ~10 nm large, the graphene thin films on the whole have very good mechanical properties and can be suspended.

We have successfully fabricated arrays of suspended-channel two-terminal devices from the graphene directly grown on 300 nm SiO_2/Si. The silicon dioxide beneath the graphene channel is locally removed by wet etching in buffered HF acid. Fig. 4 is a SEM image of a finished device. The graphene membrane is very clean without any holes or buckles. The success rate in device fabrication is nearly 100%. Suspended graphene can be used as mechanical resonators for sensitive mass sensors [11], as well as for other NEMS. Details about this type of devices can be found in another paper of this conference proceeding [12].

V. CONCLUSION

In summary, we have proposed a noncatalytic mechanism for nanocrystalline graphene CVD. The model is used to explain the formation of graphene without any metallic catalysts directly on arbitrary insulating substrates that can survive high temperature of ~1000 ^{o}C. Raman spectroscopy and TEM observation reveal the graphene nature of the synthesized thin films. The produced thin films are optically transparent, electrically conducting, and have excellent mechanical properties, resembling standard single crystal graphene. The graphene is scalable, uniform and cost-efficient. Even though the carrier mobility is much lower compared with the graphene grown by catalysis, the developed method is very promising in future industrial applications in fields such as transparent electronics, NEMS, as well as molecular electronics. Further improvements of the deposition- and fabrication techniques are underway and will be published in the future.

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