Research Letters

Synthesis, Transfer, and Devices of Single- and Few-Layer Graphene by Chemical Vapor Deposition

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Abstract—The advance of graphene-based nanoelectronics has been hampered due to the difficulty in producing single- or few-layer graphene over large areas. We report a simple, scalable, and cost-efficient method to prepare graphene using methane-based CVD on nickel films deposited over complete Si/SiO_2 wafers. By using highly diluted methane, single- and few-layer graphene were obtained, as confirmed by micro-Raman spectroscopy. In addition, a transfer technique has been applied to transfer the graphene film to target substrates via nickel etching. FETs based on the graphene films transferred to Si/SiO_2 substrates revealed a weak p-type gate dependence, while transferring of the graphene films to glass substrate allowed its characterization as transparent conductive films, exhibiting transmittance of 80% in the visible wavelength range.

Index Terms—CVD, few-layer graphene, graphene devices, graphene synthesis, graphene transfer.

I. INTRODUCTION

GRAPHENE is probably the best theoretically studied allotropic form of carbon. It consists of a 2-D hexagonal arrangement of carbon atoms, with a quasi-linear dispersion relation, for which the carrier effective mass is very low [1]. As a consequence, it has a predicted mobility at room temperatures of the order of 10^6 $cm^2/V \cdot s$ and an experimentally measured mobility of 15 000 $cm^2/V \cdot s$. The high mobility of this material opens the possibility of ballistic transport at submicrometer scales [2], [3].

Despite the advances in graphene research, and the numerous foreseen important applications, implementation of graphene has been hampered due to the difficulty of producing single- or few-layer specimens over large areas. Three main methods have been used to obtain single-layer graphene or few-layer graphene (FLG): i) epitaxial growth of graphene obtained on 6H-oriented SiC by vacuum annealing at 1400 °C [4], with the drawback of being limited by the cost and size of SiC substrates; ii) micromechanical exfoliation of small mesas of highly oriented pyrolytic graphite [3], which cannot be scaled to wafer-size dimensions; and iii) chemically assisted exfoliation of inter-calated graphite compounds [5]–[7], which typically leads to graphene with large amount of defects. An alternative way is the CVD of camphor on nickel [8], which led to the growth of graphene of about 20 layers. Camphor, however, is a solid precursor that needs to be sublimated, and its vapor pressure cannot be precisely controlled. Recently, segregation of graphene was reported on Ni surfaces; however, several layers were obtained instead of single-layer graphene, and the electronic properties of the synthesized material were not evaluated [15]. Therefore, approaches that can provide high-quality single-layer graphene and FLG over large areas and the evaluation of their electronic properties are still desired to meet realistic applications.

In this letter, we report the implementation of a simple, scalable, and cost-efficient method to prepare single-layer graphene and FLG films by CVD on nickel films by using a low molar mass hydrocarbon, such as methane, as carbon feedstock. Ni films provide an excellent geometrical fit of the ordered graphene/graphite phase of carbon to the crystalline metal surface, as well as convenient interactions that favor bond formation between carbon atoms under specific conditions [16]. It is assumed that the carbon atoms dissolve into the Ni crystalline surface, and at certain temperatures, they arrange epitaxially on the Ni (1 1 1) surface to form graphene. Synthesized graphene films on Ni were recovered on Si/SiO_2 substrates for device fabrication. In addition, we have achieved transferring the as-synthesized films to different target substrates, such as Si/SiO_2 and glass, which can enable wafer-scale silicon-compatible fabrication of hybrid silicon/graphene electronics and transparent conductive film applications.

II. EXPERIMENTAL

A. Single-Layer Graphene and FLG Synthesis

The schematic shown in Fig. 1(a) depicts the system setup employed in the CVD deposition of graphene layers. Si/SiO_2 wafers of 4-in diameter were used as substrates to deposit 100-nm-thick films of elemental Ni [Fig. 1(b)]. Evaporated films were annealed at 300 or 800 °C in a 10:1 $Ar:H_2$ mixture. Heating and cooling rates of 0.15 °C·min^{-1} allowed the formation of polycrystalline Ni domains throughout the substrate. CVD synthesis of graphene was carried out at ambient pressure by systematically varying parameters, such as temperature, gas composition, gas flow rate, and deposition time. Next, we present results obtained by heating the substrates under a flow of 600 sccm of H_2 up to 800 °C. After the target temperature
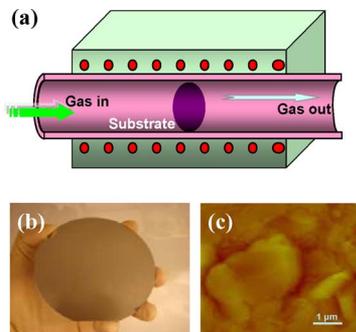
Fig. 1. (a) Schematic of full-wafer scale deposition of graphene layers on polycrystalline nickel by CVD. (b) E-beam evaporated nickel film (100 nm) on a 4 in Si/SiO$_2$ wafer. (d) AFM image of nickel film after the CVD of graphene layers.

was reached, methane gas at a flow rate of 100 sccm was added to the hydrogen flow over the substrate, which was lying horizontally inside the tube. The deposition process was conducted for 8 min. We found that using diluted methane was key to the growth of single-layer graphene and FLG (less than five layers), while using concentrated methane led to the growth of multilayer graphene that resembled bulk graphite. Our graphene growth method could be extended to other carbon feedstocks such as ethylene, acetylene, ethanol, and isopropanol, and other catalytic films such as Fe and Co.

III. RESULTS

A. Graphene Synthesis

We performed micro-Raman analysis throughout the wafers after the CVD process to confirm the formation of graphene layers on the Ni surface and to obtain information about the quality and the number of layers deposited. Fig. 2 shows Raman spectra taken at different locations on the synthesized films over Si/SiO$_2$/Ni substrates by using an excitation wavelength of 532 nm, with a power density of 2.0 mW·cm^{-2}. Strong peaks near 1580 and 2690 cm^{-1} were found. Analysis of the frequency and lineshape of these peaks allows their assignment as the G and G' bands of graphene layers, respectively [9]. The peak located at 1345 cm^{-1} corresponds to the D band of graphitic carbon species, which is associated with the amount of defects in the crystalline structure of the graphene layers. The low cross section of the D band confirms that synthesized films are largely defect-free.

Interlayer interactions affect the Raman fingerprints for single-layer graphene, bilayer graphene, and FLG, allowing unambiguous identification of graphene layers [9], [10]. Fig. 2(a) shows the Raman spectrum of single-layer graphene in the synthesized films. Single Lorentzian fit of the G' band is characteristic of monolayer graphene. On the other hand, a subtle splitting, up-shift of nearly 15 wavenumbers and broadening were observed in the G' band that can be fit with four Lorentzian peaks, as shown in Fig. 2(b), which constitute the spectroscopic signature of bilayer graphene [9], [10]. The domain size for the single-layer graphene, bilayer graphene, and FLG is typically around 1–2 μm, which is likely due to the grain size of the
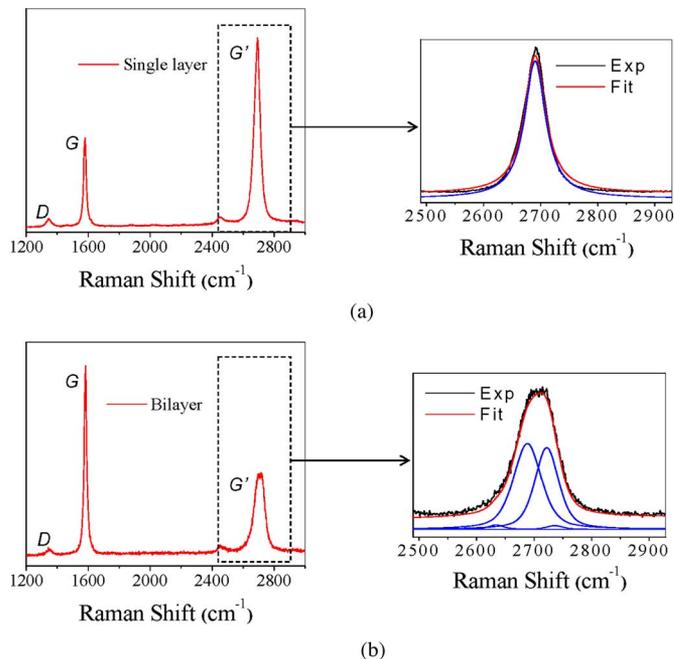

Fig. 2. Raman spectrum obtained on as-synthesized graphene films on Si/SiO$_2$/Ni substrates. D, G, and G' Raman bands for graphene are labeled on each spectrum. (a) Raman spectrum obtained on a single-layer graphene. A zoomed image of the G' band on the right shows the purely single Lorentzian fit of this peak (red trace), which is characteristic of single-layer graphene. (b) Raman spectrum of bilayer graphene. A nearly symmetric splitting and broadening of the G' band of this spectrum (shown on the right) is properly fit by a set of four Lorentzian curves, characteristic of bilayer graphene. No G' band was found with a bulk graphite-like lineshape on the substrates sampled.

polycrystalline nickel film. Extensive Raman characterization over as-synthesized samples consistently showed the presence of graphene with less than five graphene layers [11]. No signature of multilayer or bulk graphite was found in the films deposited.

B. Electrical Measurements and Transparency

Two methods were used to transfer the as-synthesized graphene film to target substrates. The first approach consisted of immersing the graphene-on-nickel sample into a nickel etchant solution [Fig. 3(a)]. This process removed nickel and left graphene films deposited on the underlying Si/SiO$_2$ substrate. Fig. 3(b) shows a photograph of an Si/SiO$_2$/Ni/Graphene wafer right after CVD synthesis (upper left). Micro-Raman spectrum taken on the films after transfer is shown in the lower left part of Fig. 2(b), clearly showing very low D-band intensity. This confirms that graphene is largely defect-free after transfer. Upper and lower right panels of Fig. 3(b) show atomic force microscopy (AFM) and white light microscopy images of the graphene films on Si/SiO$_2$ substrate after etching the Ni film, respectively. FLG were composed of micrometer-scale domains of single-layer graphene, bilayer graphene, and FLG with a maximum thickness of five layers, as confirmed by micro-Raman spectroscopy. This allowed the fabrication of back-gated FETs on large scale [Fig. 3(c)]. Micro-Raman measurements performed on the device channel were consistent with a maximum
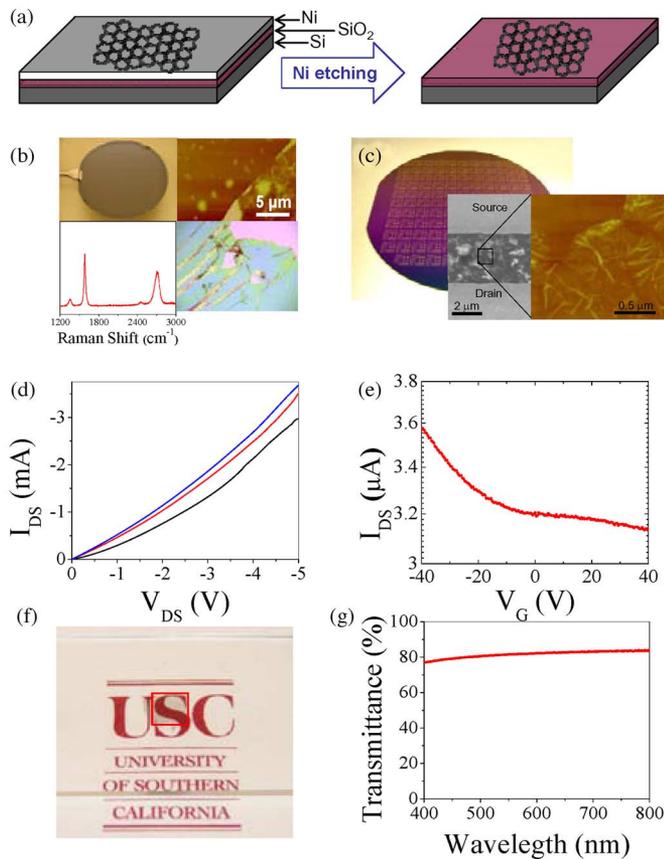
Fig. 3. (color online). (a) Schematic of a graphene film transferred to a Si/SiO$_2$ substrate via nickel etching. (b) Photograph of a 4-in wafer after synthesis of transferred FLG on polycrystalline nickel; (upper right) shows an AFM image of the few-layer graphene films on Si/SiO$_2$; (lower right panel) shows an optical micrograph of deposited few-layer graphene on Si/SiO$_2$; (lower left panel) shows a typical micro-Raman spectrum of the transferred films. (c) 4-in wafer with back-gated few-layer graphene devices; insets show SEM and AFM images of a device and device channel, respectively. (d) I_{DS}–V_{DS} measurements for different gate voltages, $V_G = 2.5$ V, 1.5 V, and -1.5 V for the black (lower), red (middle), and blue (upper) curves, respectively, and (e) I_{DS}–V_G curve of one of the FET devices for $V_{DS} = 0.01$ V. (f) Photograph of a 1 cm^2 FLG film transferred onto a glass substrate (inside the box). (g) Transmittance of the FLG film shown in (f).

of five graphene layers comprising the films (data not shown). Four-probe measurements performed on the FLG films revealed a sheet resistance of $\sim$68 kΩ/square. $I_{DS} - V_{DS}$ characteristics depicted in Fig. 3(d) show that the drain current increases with the increase of negative gate voltage, indicating a weak p-type behavior in the films. Fig. 3(e) shows the transfer characteristics for a device with a channel width of 20 μm and channel length of 4 μm. Most devices were highly conductive and exhibited a weak modulation of the drain current by the gate bias, which is consistent with a 2-D semimetal [3]. Compared to nanotubes [13], [14], graphene FETs typically exhibit low ON/OFF ratios, which can be improved significantly by patterning graphene into nanoribbons [14]. Single-graphene layer is a zero-gap semiconductor, but interlayer interactions bring in a semimetal behavior in FLG. Therefore, the transfer characteristics observed in Fig. 3(e) can be attributed to a screened gating effect due to irregularities of the film and the presence of more than two graphene layers in the films.

For our second transfer approach, we used poly(methyl methacrylate) (PMMA), which was spin-coated on top of the synthesized graphene films lying on Si/SiO$_2$/Ni substrates. The wafer was dipped into a nickel etchant solution (Transene Company, Inc.) at 90 °C for 2 h to etch away the nickel film and render a free-standing PMMA film with the synthesized graphene adhered to it. PMMA/graphene film was transferred to other substrates (Si/SiO$_2$, glass, etc.), and then acetone was used to dissolve the PMMA residues and leave clean graphene films on the target substrate surface. Fig. 3(f) shows a photograph of a $\sim$1 cm^2 FLG film transferred on glass exhibiting high transparency to naked eyes. PMMA-assisted transfer is currently limited to small areas due to the difficulty in handling PMMA films; however, we are certain that wafer-scale transfer by similar approaches using PMMA or other polymers will be developed. Fig. 3(g) shows that the transmittance spectrum of the transferred FLG film in the visible wavelength range is $\sim$80%, which is consistent with the visible light transmittance reported for 2–3 graphene layer films [12]. Due to the simultaneous good electrical conductivity and high transparency of the synthesized graphene films, they are likely to find application as transparent conductors.

In summary, this letter demonstrates a simple, scalable, and effective method to synthesize monolayer and few-layer graphene films by using methane-based CVD on nickel films, transfer of the synthesized films to different target substrates, and their evaluation as transparent conducting films. Graphene produced over Si/SiO$_2$ wafers can be very useful for device fabrication, and our approach may serve as the foundation for the growth of single-domain graphene over macroscale areas such as complete wafers. Growth of graphene on single-crystalline nickel is currently underway with the goal of significantly increasing graphene grain size. This approach constitutes a significant advance toward the production of thin films of graphene at industrial scales and has important implications for future graphene-related electronic devices.

Note Added after Xplore Online Publication

During the review of the present paper we became aware of a related paper entitled "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition" by A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus and J. Kong, Nano Lett. (online publication Dec. 1, 2008). They independently reported a CVD approach to produce few-layer graphene on nickel surface. That report is in good agreement with the results shown here. We not that our paper, to the best of our knowledge, is the first report on CVD synthesis of graphene layers over complete wafers.

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