Large Scale Graphene Films Synthesized on Metals and Transferred to Insulators for Electronic Applications

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Graphene\textsuperscript{1} has attracted tremendous recent interests as an electronic material with exceptional properties that may enable a new generation of nanoelectronics and functional devices. The availability of high quality, large-size graphene samples\textsuperscript{2-7} is important for many practical applications. For decades, graphene (down to a monolayer) has been successfully grown by chemical vapor deposition (CVD) or related surface segregation on various metal substrates\textsuperscript{8-10}. However, the electronic properties and device applications of such CVD graphene have been largely unexplored. Here we report ambipolar electric field effect and quantum transport in large-scale, few-layer graphene films transferred to Si/SiO\textsubscript{2}, after being grown on Ni under ambient pressure by non-equilibrium surface segregation\textsuperscript{11}. We demonstrate carrier mobility reaching 2000 cm\textsuperscript{2}/Vs and phase coherence length over 0.2 \textmu m. Such wafer-scale graphene films can be transferred\textsuperscript{11} on a variety of substrates and open many application possibilities for carbon-based electronics.
Our method to grow few-layer graphene films on polycrystalline Nickel (Ni) has been described in detail previously\textsuperscript{11}. The growth is based on a non-equilibrium surface segregation process by controlled cooling, carried out in a chemical vapor deposition (CVD) chamber under ambient pressure. Briefly, we dissolve carbon (decomposed from precursor gases containing hydrocarbon, such as CH\textsubscript{4}) into bulk Ni (serving also as a catalyst) at ~\textdegree{}1000, followed by cooling with appropriate rates\textsuperscript{11} to room temperature. During the cool-down, carbon solubility in Ni decreases and carbon segregates at the surface of Ni substrate to form graphene layers. Previous studies\textsuperscript{11} have shown that few-layer graphene films of high quality (as confirmed by transmission electron microscopy (TEM), Raman scattering and X-ray photoelectron spectroscopy (XPS)) can be grown by such a method and transferred to other substrates. The thickness of the film grown is found to depend sensitively on many experimental parameters, including the cooling rate\textsuperscript{11}. Moreover, similar to most other types of macroscopic graphene films grown epitaxially or chemically to date, the thickness is generally non-uniform at large scale. For example, we can often find regions as thin as \textless{}~2 layers of graphene\textsuperscript{11} and as thick as tens of layers in the same sample. Despite this macroscopic non-uniformity, such ultrathin films can have good electronic quality for many applications, as shown below.

Transferring as-grown graphene films from metals to insulator substrates is a critical step for fabricating electronic devices. In this work, we have used a simple method of substrate transfer, without the need of any auxiliary adhesive or supportive coatings. The Ni substrate with as-grown films is placed in an acid solution, where the graphene film detaches from Ni and floats on top of the liquid surface. This is demonstrated in Fig. 1a for a large film, close to 1 cm in size and largely-transparent. The film can then be
simply skimmed out by the insulator substrate onto which it is transferred (Fig. 1b). The type of insulator substrate used in this work is 300nm SiO$_2$ on doped Si wafer.

Fig. 2a and its inset (magnified 3D view) shows a high resolution scanning tunneling microscopy (STM) image measured in a film transferred onto SiO$_2$ with the above acid-based approach. The film is connected with conducting tapes to provide a current return path in STM measurements. The hexagonal pattern of the underlying graphitic lattice is clearly revealed down to atomic levels. Fig. 2b is a lower resolution STM image, showing tall ridges (height ~60-100 nm) separating relatively flat regions. These ridges are wrinkles on the film and can be seen even under optical microscopes. Although some wrinkles are found to be introduced during the transfer process, many of them are already present before the transfer, as shown in the atomic force microscope (AFM) image (Fig. 2c) of an as-grown film on Ni substrate. The height of some of the larger wrinkles can reach ~100 nm (Fig. 2d), at least an order of magnitude larger than those of the thickness fluctuations in the graphene layers as well as substrate roughness of Ni. These wrinkles may mostly be attributed to the larger thermal contraction coefficients of Ni (12.9~21.0×10$^{-6}$ K$^{-1}$)$^{12}$ than that of graphene (0.7~1.2×10$^{-6}$ K$^{-1}$)$^{13}$ during the growth (cool-down) process.

To characterize the electronic properties of the transferred graphene films, we have patterned them into relatively large-size Hall-bars with multiple contact electrodes (Cr/Au). The devices were fabricated by standard optical lithography, plasma etching and metal deposition. The optical microscope image of a typical device is shown in Fig. 3a, and the schematic cross-section in Fig. 3b. We have mainly performed two types of electronic measurements at various temperatures: 1) field effect (transistor)
measurements, where the heavily doped Si wafer is used as the back gate; 2) magneto-transport measurements, where a perpendicular magnetic field is applied to the film.

Fig. 3c shows 4-terminal resistance measured in a device (“A”) at low temperature ($T = 10$ K), where the back gate voltage ($V_{\text{gate}}$) is varied between -90 V to 60 V. An ambipolar field effect is evident, where the resistance can be modulated by more than 50%, with its peak ("charge-neutral point") occurring at \( \sim 10 \) V. Similar field effects are observable up to room temperature, though at low $T$, larger range of $V_{\text{gate}}$ can be accessed without gate leakage. The insets (Fig. 3d and 3e) show Hall effects measured at $V_{\text{gate}} = -20$ V and 40 V respectively, with opposite signs of Hall slope observed. Such a sign-change in the Hall effect is another hall-mark of the ambipolar field effect and is so far only observed in ultrathin 2D graphitic systems, where electronic transport in the field effect is dominated by only few graphene layers$^{14-16}$. This also directly shows that our film can be electrically doped from p-type (Fig. 3d) to n-type (Fig. 3e). The extracted carrier mobility for $V_{\text{gate}}$ far away from the charge neutral point is \( \sim 1000-2000 \) cm$^2$/Vs. Although the mobilities in our samples and the “on/off” modulation ratio in the ambipolar field effect are still rather moderate, they may already be valuable for certain applications, especially in analog electronics with carbon-based RF and high speed devices$^{17,18}$.

Fig. 4a shows the magneto-resistance $\Delta R_{xx}(B) = R_{xx}(B) - R_{xx}(B = 0 \text{ T})$ measured between -0.4 T and 0.4 T in a device (“B”) at several temperatures. At low temperature (eg., $T = 0.5$ K), we observe a pronounced low field negative magnetoresistance (with a peak in $R_{xx}$ at $B = 0$ T), which weakens at elevated temperatures and disappears at sufficiently high $T (\sim 20$ K). Such features are characteristic of the so called “weak-
localization” (WL)\(^{19}\), and have been observed in many other graphitic systems\(^{20-24}\). WL arises from the constructive quantum interference between time-reversed multiple-scattering trajectories (within a length scale \(L_\varphi\) that electron wave function is phase coherent) that enhances the probability of electron localization (thus also the electrical resistance). Such a WL can be destroyed by magnetic field (which breaks the time-reversal symmetry) or high temperature, giving rise to the observed negative magnetoresistance at low \(T\). We found that our data can be well described by the standard 2D WL theory\(^{19}\). For example, the inset 4b shows the measured WL correction in the magnetoconductivity \(\Delta \sigma(B) = \sigma(B) - \sigma(B = 0\, T)\) at 0.5 K, fitted to the theoretically predicted form\(^{19}\) for 2D diffusive metals,

\[
\Delta \sigma_{\text{WL}}(B) = \left( 2e^2 \pi h \right) \left[ F\left( \frac{8\pi B}{(h/e)L_{\varphi}^2} \right) - F\left( \frac{8\pi B}{(h/e)L_{tr}^2} \right) \right],
\]

where \(e\) is electron charge, \(h\) is the Planck constant, \(F[z] = \ln(z) + \Psi(1/2 + 1/z)\) with \(\Psi\) being the Digamma function, \(L_\varphi\) is the afore-mentioned phase coherence length, and \(L_{tr}\) is the transport scattering length.

Excellent fit (\(L_\varphi\) and \(L_{tr}\) being the two fitting parameters) has been obtained for the entire range of measured data for all temperatures at which we observe WL. Inset 4c shows \(L_\varphi\) and \(L_{tr}\) extracted from such fits, plotted against the temperature. \(L_{tr}\) is found to be largely temperature-insensitive in the measured range, and its value is on the similar order of magnitude as the transport mean-free path (~30-60 nm) extracted from the mobilities. The phase coherence length \(L_\varphi\) is seen to steadily rise as \(T\) is lowered, reaching above 0.2 \(\mu\text{m}\) at low \(T\) (0.5 K). The \(L_\varphi\) is much smaller than the size (~100 \(\mu\text{m}\)) of our devices, consistent with the diffusive limit. On the other hand, we envision that phase coherent or ballistic transport may be explored in much smaller submicron devices fabricated from
our CVD graphene films. WL has received strong attention in recent studies of both exfoliated\textsuperscript{21,23-26} and epitaxially grown (on SiC)\textsuperscript{3,4,22,27} graphene systems. A host of important information on the scattering and quantum transport of carriers, as well as about disorder in the samples, can often be obtained by careful analysis of WL. Such information can be valuable to design and improve graphene-based electronics\textsuperscript{2-4} --- including novel quantum coherent devices\textsuperscript{28,29}, where phase coherent electron transport is utilized for new device functionalities or improved performance.

In sum, the transferred CVD graphene films represent a new class of graphene-based electronic materials that can be produced at low cost, in large scale and quantity, and on almost arbitrary substrates. Their electronic properties are shown here to be rather good (given the large sizes and surface roughness of the samples we studied) and can enable many applications, ranging from thin film transistors, high speed/high frequency devices\textsuperscript{17}, conductive coatings, to transparent\textsuperscript{30} or flexible electronics.

\textit{Note added.} After our work was completed, we became aware of a recent report\textsuperscript{32} of related work, which also demonstrated an electric field effect in CVD-grown graphene films.

\textbf{References}


15. Zhang, Y., Small, J. P., Amori, M. E. S. & Kim, P. Electric field modulation of 
   (2005).

16. Morozov, S.V. et al. Two-dimensional electron and hole gases at the surface of 

17. Lin, Y.M. Operations of graphene transistors at GHz frequencies, 


   (2007).

   176805 (2007).


32. Reina, A. *et al.* Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* in print (2009); published on-line (ASAP) and available at DOI: 10.1021/nl801827v

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**Author contributions**

YPC and QY conceived the project. HC fabricated the devices and performed electronic transport measurements, the data from which were analyzed by HC and YPC. QY synthesized and transferred the graphene films. HC, QK, DP, DZ, IC, RC and VD performed various microscopy and surface analysis of the graphene films. All authors contributed to the scientific planning and discussions. YPC coordinated the research and wrote the paper.

**Competing financial interests**

The authors declare no competing financial interests.
Fig. 1. Photographs of large scale graphene film transferred to insulator substrate. (a) A large-size film floating on the surface of the acid solution (HNO₃) used to etch the film off its growth substrate (Nickel). A pair of tweezers is placed behind the largely-transparent film. (b) The film in (a) transferred onto a Si/SiO₂ wafer.
Fig. 2. Structure and surface characterizations. (a) High resolution scanning tunneling microscope (STM) image of a film transferred onto Si/SiO₂ substrate, revealing the underlying hexagonal graphitic lattice structure. A wavelet-based filter\textsuperscript{31} is used to enhance the contrast of atomic images. Inset shows a 1.25 nm x 1.25nm magnified 3D view. (b) Low resolution STM image of the film in (a), with relatively flat domains separated by tall ridges/wrinkles (tens of nm in height). (c) Atomic force microscope (AFM) image (phase-contrast) of an as-grown film on Ni (before transferring), showing the topography of the wrinkles/ridges on the “crumbled” film. (d) Cross sectional height profile corresponding to the dashed line in (c), through two large wrinkles.
Fig. 3. Electronic devices and ambipolar field effect. (a) Optical microscope image of a typical field effect transistor (FET) device (top view) fabricated from a large scale transferred film, patterned into the Hall bar shape by photolithography. (b) Schematic diagram (not to scale) of the cross section of a FET device. (c) Four-terminal resistance as a function of back gate voltage ($V_{\text{gate}}$), showing the electric field effect. (d) Hall effect (Hall resistance as a function of perpendicular magnetic field) measured at $V_{\text{gate}} = -20$ V, showing a positive sign and predominantly p-type carriers. (e) Hall effect measured at $V_{\text{gate}} = 40$ V, showing a negative sign and predominantly n-type carriers. Data in (c, d, e) are measured in the same sample (“A”) at a temperature of 10 K.
Fig. 4. Quantum transport and weak localization. (a) Magnetoresistance $\Delta R_{xx}(B) = R_{xx}(B) - R_{xx}(0T)$ at several temperatures. $R_{xx}$ is the four-terminal (longitudinal) resistance. (b) Magnetoconductivity (normalized by $e^2/h$) $\Delta \sigma(B) = \sigma(B) - \sigma(0T)$ at 0.5 K. Empty circles are measured data (after subtracting a high temperature background to extract the WL correction). Solid line is the fit using the 2D WL theory\(^{19}\) (see text). (c) Extracted phase coherence length (filled circles) and transport scattering length (empty squares) as a function of the temperature.