30 Inch Graphene and the Origin of Electron-Hole Puddles

"Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils"
Authors: X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff
HYPERLINK "http://dx.doi.org/10.1126/science.1171245"Science **324**, 1312 (2009)

"30-Inch Roll-Based Production of High-Quality Graphene Films for Flexible Transparent Electrodes"
Authors: S. Bae, H. K. Kim, X. Xu, J. Balakrishnan, T. Lei, Y. I. Song, Y. J. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, S. Iijima
HYPERLINK "http://lanl.arxiv.org/abs/0912.5485" arXiv:0912.5485

"Origin of spatial charge inhomogeneity in graphene"
Authors: Y. Zhang, V. W. Brar, C. Girit, Alex Zettl, M. F. Crommie
HYPERLINK "http://dx.doi.org/10.1038/NPHYS1365" Nature Physics **5**, 722 (2009)

Recommended with a commentary by Roland Kawakami,

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The past several months have witnessed exceptional progress in graphene research, solving two important problems: (1) making large area single-layer graphene and (2) determining the origin of electron-hole puddles observed under charge neutral conditions (HYPERLINK "http://www.condmatjournalclub.org/?p=500" highlighted in this journal club in July 2007). Although these issues appear unrelated, there is an important connection discussed below.

A breakthrough in graphene research over the past year is the ability to grow large areas of single-layer graphene (X. Li et. al.), culminating in the synthesis of a 30 inch sheet (S. Bae et. al.). Until recently, most of the research has been based on small flakes (tens of microns) exfoliated from graphite by scotch tape. The new method is chemical vapor deposition onto copper foil at ~1000°C using precursor gas of methane + hydrogen at ~1 Torr. The graphene is then supported by a polymer, the Cu foil is etched away, and the graphene can be transferred to any substrate. The amazing fact is that over 90% of the graphene film is single-layer. This is having a major impact on condensed matter research as many groups have reproduced this result (most are unpublished) and are incorporating it into their research programs. Technologically, this opens the door to applications in high speed rf circuits and transparent electrodes for solar cells and flat panel displays.

A second important result is a scanning tunneling microscopy (STM) study to identify the origin of electron-hole puddles (Y. Zhang et. al.) that were first observed by scanning single-electron transistor (SET) microscopy [Martin et. al., Nature Phys. 4, 144 (2008)]. The puddles appear when the graphene is electrostatically tuned to the Dirac point for a charge neutral condition. While it has been attributed to disorder, the nature of the disorder has been unknown. In the work by Zhang et. al., STM spectroscopy (dI/dV vs. sample bias) is performed on graphene on a SiO_2/Si substrate and the Dirac point is identified by the minima in the dI/dV spectra. The carrier concentration is then determined by the voltage at which the Dirac point appears, with Dirac point below (above) the Fermi level corresponding to electrons (holes). By mapping out the carrier concentration across the sample, electron-hole puddles of average size of about 20 nm are identified. The important question is the origin of these electron-hole puddles. The atomic scale resolution can identify lattice vacancies and impurities on top of graphene—apparently these are not the source of electron-hole puddles. What about corrugations in the graphene topography, or "ripples"? Comparing the ripples and the electron-hole puddles shows no correlation, so it is not the ripples. Finally, a dI/dV map at high sample bias identifies the presence of charged impurities located under the graphene. Comparing the position of these charged impurities with the electron-hole puddles show a strong correlation, so it appears that the origin of the electron-hole puddles are charged impurities located underneath the graphene sheet.

This study also makes a surprising observation of backscattering of the carriers, which is supposed to be prohibited because the counter-propagating electron states on opposite sides of the Dirac point do not have a matching wavefunction symmetry ("prohibited by conservation of pseudospin" in the graphene jargon). This is identified by the standing wave patterns in dI/dV maps taken at different biases and seen more clearly in their

Fourier transforms. Understanding the nature of the backscattering is an interesting topic that relates to the ultimate mobility in graphene.

The presence of charged impurities between the graphene and SiO_2 may either be due to trapped air molecules or by impurities or defects related to the SiO_2 itself. Because this produces electron-hole puddles and reduces the mobility, one would like to use a different substrate with fewer defects and impurities. However, most researchers still use SiO_2/Si substrates due to the ease of identifying the single layer graphene by optical microscopy. It might also be necessary to lay the graphene on the substrate while in vacuum to avoid trapping gas molecules. The large area graphene produced by CVD could become very important for dealing with the problems identified by the STM study. This graphene can be transferred to a higher quality substrate and the procedure could be performed in vacuum relatively easily. Thus, the CVD method provides a route to eliminate the electron-hole puddles and to achieve higher mobilities on insulating substrates.

The presence of charged disorder in the SiO_2 is a second strike against the SiO_2/Si substrate, the first being a mobility limitation due to surface phonons in the SiO_2. But apart from removing the substrate altogether in suspended graphene, most researchers still use SiO_2/Si substrates. Why? Because the single-layer graphene is readily identified by optical microscopy due to the well-known optical interference that makes single-layer graphene on SiO_2/Si appear with a faint purple hue. This is where the large area graphene by CVD on Cu can help. In this process, the single-layer graphene can be transferred to any substrate. Since the graphene covers the entire substrate, there is no need to locate the single-layer graphene. This frees graphene researchers from the SiO_2/Si substrate, allowing one to use cleaner substrates or ones with novel functionality (e.g. magnetic, optical, etc.).