Conjugated Carbon Monolayer Membranes – Synthesis and Integration Techniques

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The existence of graphene,¹ a single sheet of graphite and the simplest class of conjugated carbon monolayer, discovered in 2004, has attracted immensely interests from scientific community. The research in this area has grown exponentially attributed to its exceptionally high electron mobility,² high elastic moduli,³ and observations of unconventional phenomena in physics.⁴ Unfortunately, the original technique for producing graphene sheet on insulating substrates, i.e. by mechanical exfoliation using Scotch tape, from a piece of graphite is not scalable. Hence, it is utmost important to investigate for other approaches for producing large area graphene and/or improving the quality of film transfer technique. It is as well interesting to explore other types of related two-dimensional materials.

The first part of this seminar describes a strategy for the synthesis of a class of conjugated carbon monolayer membranes.⁵ The strategy involves the formation of self-assembled monolayer of alkyne-containing monomers on flat or structured solid support such as SiO_2 and Si_3N_4 followed by chemical crosslinking within monolayer. Once linked, the membranes are robust enough to be released from the support and transferred to other surfaces. Likewise, three-dimensional objects, such as balloons and cylinders, with monolayer thickness can be generated with similar method as shown in Figure 1.

Other approaches for mass production of graphene are under active investigation.⁶ These include epitaxial growth on SiC substrates, chemical vapor deposition growth on metal surfaces, and chemical reduction of graphene oxide (GO). The first method relies on Si sublimation and graphization of C atoms on the SiC by annealing at high temperature under ultra high vacuum (UHV). This approach is promising, but its current implementation requires the use of SiC as the device substrate due to lack of transfer method. This feature frustrates integration with silicon technologies, and requires the use of top gate transistor device geometries.

This second part of the seminar focuses on developing a transfer technique to transfer graphene films grown on SiC substrates to other arbitrary substrates. The process utilizes a bilayer film of either gold/polyimide⁷ or palladium/polyimide⁸ as a transfer element. In case of using palladium, single layers of graphene are transferred over large areas with high yields. Interestingly, this process can be repeated to enable a layer-by-layer transfer of multiple, large area sheets of graphene from a single SiC substrate (See Figure 2). Finally, various measurements on the films before and after transfer from SiC, ranging from low energy electron diffraction (LEED), to X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning tunneling microscopy (STM), and electrical measurement are presented.



Figure 1: Images of "unusual" monolayer membrane structures. (A and B) SEM and AFM images, respectively, of a linked monolayer membrane transferred onto a substrate with a square array of cylindrical holes to form "drumhead" structures. Red arrows point to the same region of the film that is suspended over the edge of a hole. (C and D) AFM and high-resolution AFM images, respectively, of a monolayer membrane grown on a substrate similar to that in A, but with relief depths of ≈ 35 nm, and then transferred to a flat Si wafer with a 300-nm thermal SiO₂ layer. (C Inset Upper Left) Power spectrum of the AFM image, indicating a well defined periodicity consistent with that of the growth substrate. (C Inset Lower Right) Illustration of a "pleated sheet." (E and F) TEM images and diameter distributions of a monolayer membrane deposited on SiO₂ spheres imaged on a holey carbon-coated grid before (E) and after (F) HF vapor etching of the SiO₂. Insets are illustrations of the imaged structures. (G–I) Time-resolved optical micrographs of a tubular membrane filled with HF/water immediately after HF vapor etching of optical fiber, after 20 min open to the air, and after complete drying, respectively. Insets are illustrations of the image of this collapsed tube. The line scan corresponds to an average over the area indicated by the rectangle.



Figure 2: (A) An image from a digital camera showing two transferred graphene films transferred from a SiC growth substrate to two SiO₂/Si substrates. The films are uniform over square centimeter. (B) An optical image of a graphene sheet in (A) taken at the film edge

References

- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, *306*, 666-669.
- Bolotin, K. I.; Sikes, K. J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H. L. Ultrahigh Electron Mobility in Suspended Graphene. *Solid State Commun.* 2008, 146, 351-355.
- 3. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* **2008**, *321*, 385-388.
- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov A. A. Two-dimensional gas of massless dirac fermions in graphene. *Nature* 2005, 438, 197-200.
- Schultz, M. J.; Zhang, X.; Unarunotai, S.; Khang, D.-Y.; Cao, Q.; Wang, C.; Lei, C.; MacLaren, S.; Soares, J. A. N. T.; Petrov, I.; Moore, J. S.; Rogers, J. A. Synthesis of linked carbon monolayers: Films, balloons, tubes, and pleated sheets. *Proc. Natl. Acad. Sci. USA* 2008, 105, 7353-7358.
- 6. Unarunotai, S.; Murata, Y.; Chialvo, C. E.; Mason, N.; Petrov, I.; Nuzzo, R. G.; Moore, J. S.; Rogers, J. A. Conjugated Carbon Monolayer Membranes: Methods for Synthesis and Integration. *Adv. Mater.* **2010**, *22*, 1072-1077.
- 7. Unarunotai, S.; Murata, Y.; Chialvo, C. E.; Kim, H.-S.; MacLaren, S.; Mason, N.; Petrov, I.; Rogers, J. A. Transfer of Graphene Layers Grown on SiC Wafers to Other Substrates and Their Integration into Field Effect Transistors. *Appl. Phys. Lett.* **2009**, *95*, 202101.
- 8. Unarunotai, S.; Koepke, J. C.; Tsai, C. L.; Du, F.; Chialvo, C. E.; Murata, Y.; Haasch, R.; Petrov, I.; Mason, N.; Shim, M.; Lyding, J.; Rogers, J. A. *In preparation*.