Scotch Tape, N°2 Pencils and Batteries: Junk Drawer or the Makings of a Superconductor?

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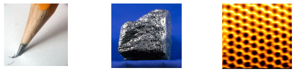
Introduction

Graphite, i.e. the “lead” in most pencils

- Most stable form of pure carbon under standard conditions.
- Structurally, formed from layers of carbon sheets, resembling a stack of honeycombs, held together by weak interactions.



Left. Pencils deposit flakes of mult-layer graphene on paper every time we write (mrsec.wisc.edu)
Middle. Chunk of graphite (us.gov)
Right. AFM image of carbon atom network in graphite (physik.uni-augsburg.de)

Graphene is the name of a single layer

- Can be prepared by mechanical exfoliation – when graphite is placed on a piece of scotch tape and pulled apart until a single layer can be isolated.
- An electric field can be applied to graphene and shift the Fermi level, having a direct consequence on its electronic properties.

Motivation

Graphite intercalation compounds with metal cations have shown **superconductive** behavior.

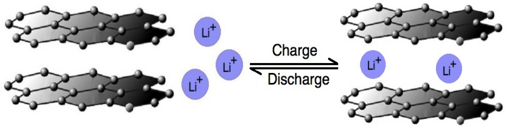
- Transition temperatures (T_c) as high as 11.5 K for CaC_6.
- Theoretical work predicts similar instabilities in graphene if the right electric field is applied.
- Methods such as bottom and top-gating, while increasing the Fermi level, have not been successful enough to observe this phenomenon.
- Chemical doping is a likely alternative but the techniques typically used are limited.
- Electrochemistry can prompt reluctant reactions.
- Exfoliation of graphene allows for more control in the number of layers of a given sample.
- This combined with electrochemistry gives us great control over sample preparation.

Goals

- We intend to observe the dependence between the number of graphene layers in our samples and the Raman spectra collected during intercalation.
- As intercalation can occur in stages, depending on the amount of intercalate sandwiched between layers and between which layers, we intend to identify the spectra corresponding to each within our setup.
- With this we should be able to correlate the Raman spectra with conductivity and therefore transport measurements such as the quantum Hall effect.
- With a recipe in hand, we will move on to other cations, focusing specifically on those that have shown superconductivity with graphite as well as magnesium which to this day has yet to be intercalated in either bulk graphite or graphene.

Intercalation via Electrochemistry:

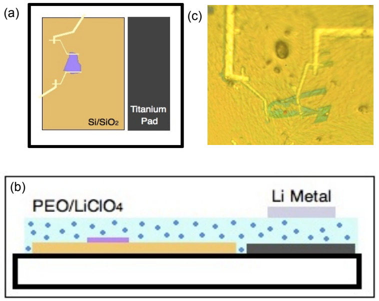
- Analogous to a rechargeable battery:
  - While discharging, a spontaneous chemical reaction will occur, creating electricity, and powering a device.
  - While charging, electricity is used to drive the reaction in the reverse direction so that the battery can be used again.
- Similarly, we use a technique known as chronoamperometry to apply constant DC voltage to graphene and drive the intercalation forwards.
- Lithium ions chosen as a first step primarily due to ubiquity in electrochemical studies.



Schematic portraying the intercalation of Li^+ in between two layers of graphene: Upon the application of an increasingly negative potential to graphene, the lithium ions will sandwich themselves between layers. When the potential is allowed to return to it's original state, the lithium ions travel back out from in between the layers of graphene.

Device and Experimental Design:

- Graphene exfoliated onto Si/SiO_2 wafer
- Once processed and contacts are laid down, the wafer is placed on a stage, alongside a titanium pad. (See figure (a) to right.)
- The device is brought into an inert atmosphere (Ar-filled glove box) along with the sample chamber.
- The eltrochemical cell is prepared by drop-casting a dry (i.e. water-free) solution of poly(ethylene) oxide (**PEO**) with $LiClO_4$ as the electrolyte.
- A piece of lithium metal is then deposited on top, to act as both counter and reference electrode. (Figure (b) to right.)
- Once secured and sealed in the sample chamber, the entire chamber is transferred out of the glove box and attached to a potentiostat.
- An optical image of one such device can be seen in (c). Discoloration around the edges and moving inward is observed over time. This is probably due to unavoidable reduction products from the polymer and electrolyte.

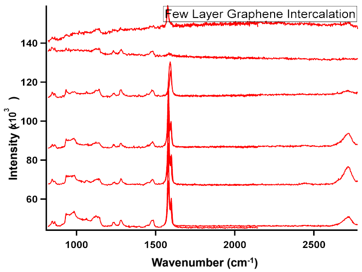


Observing Intercalation: Raman Spectroelectrochemistry

The sample chamber has a window, allowing us to do Raman spectroscopy while controlling the potential in the device electrochemically.

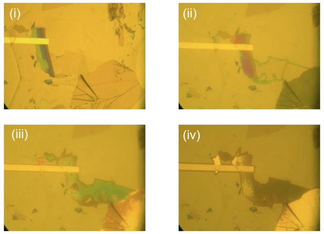
Evolution of the graphene G peak and 2D peak:

- The bottom-most spectrum is of the device with no external potential applied. Both peaks are present at full intensity.
- The next three spectra were recorded successively, at various times during the intercalation process.
- The two graphene peaks decrease in intensity until finally, as can be seen in the spectrum that is second from the top, the peaks disappear into the baseline.
- The top-most spectrum is of the device after ample discharge. The graphene peaks reappear.



Spectra courtesy of Yinsheng Guo, Brus Group

Optical Changes During Intercalation:

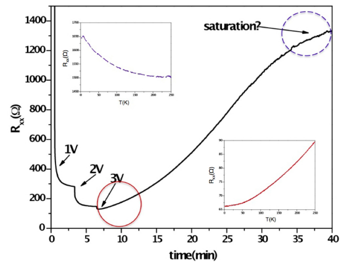


Optical images of a sample containing bulk graphite, multilayer and single layer graphene:

Snapshots at sequential points during intercalation. Time increases from (i) to (iv). (i) is deintercalated.

Optical images courtesy of Yinsheng Guo, Brus Group

Preliminary Transport Data



Single Layer Graphene at 3V and 310 K

- n = 8 x 10^{13} when cooled after 3V achieved
- n= 8.7 x 10^{13} cooled after waiting at 3 V until 40min
- despite opposite trend in R_{xx} as a function of T

Absolutely reversible if warmed & cooled again

Data Courtesy of Dmitri Efetov, Kim Group

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