Graphene – Searching For Two Dimensions

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It is thought that every time someone uses a pencil, they are creating one of the most expensive materials on the earth.(1) Not only that but also the thinnest material on earth. Graphene is the quasi two-dimensional equivalent of three-dimensional graphite. Graphite is comprised of approximately four-angstrom thick layers of graphene stacked upon it self. The bonds between the carbon atoms in the honeycomb lattice of 1.42 angstroms of graphene are extremely strong compared to the bond strength between the layers, which is rather weak.(2)(5) This is what makes graphite such a great lubricant but gives graphene unusual and exciting properties.

Perhaps the most interesting aspect of graphene is the way the electrons are described within the lattice. In most condensed matter, electron transport is described by the Schrodinger equation. This is not the case for graphene, which is described by the Dirac equation.(3) For graphene, the energy-momentum relation is linear near the six corners of the Brillouin zone described by equation 1. This allows the electrons to move with zero effective mass near these Dirac points. The fermi velocity for these Dirac fermions is 10^6m/s, which is still a factor of 300 off of the speed of light yet still considered relativistic.(3)(4)(5)

Besides having the smallest resistivity of any other material known on earth, graphene also has a minimum conductivity. From before, the effective mass of electrons at the Dirac points is zero; therefore the carrier density at these points should also be zero.(2)(5) Consistently, researchers have observed a minimum conductivity described in equation 2. The origin of this minimum conductivity is still unclear but a large subject of current research. Theorists predict another factor of $1/\pi$ despite researchers continued measurements.(5)

The quantum Hall effect is yet another amazing property of graphene. The Hall effect is the potential difference on the opposite sides of an electrical conductor through which an electric current is flowing, created by a magnetic field applied perpendicular to the current. The quantum Hall effect is the two-dimensional equivalent with quantized values of conductivity. Bi-layer graphene follows the general equation, as seen in equation 3, as monolayer graphene is shifted by a factor of ½ in a new half-integer quantum Hall effect seen in equation 4.(4) While this can only be observed in extremely low temperature, graphene is the only known material that exhibits this behavior at room temperature.(4)(5)

Graphene is exciting so many people, not only for its current research, but also for what it may hold for the future. Quickly becoming the leading candidate to replace silicon, graphenium microprocessors would increase the performance of computers by an order of magnitude better than silicon.(5) Furthermore, silicon transistors have become almost as small as they can and still work effectively. Graphene transistors, which have already been created, not only work well on small scales but also actually work better the smaller they become.(7)(8) Replacing carbon nanofibers with graphene powder in batteries would greatly increase the effectivness of batteries to be possibly used in cars lessening the dependence of oil. Graphene is currently being tested in sensors since it has the ability to detect even a single molecule of gas.(5)(6)

The reason graphene isn't being incorporated into companies like Intel, despite their public interest, is because mass production is still not available which has lead to its status as the most expensive material on earth.(2) I spent the summer in Dr. David Cobden's lab trying to create and find single layer graphene for research purposes. This is where the title comes from since this seemingly simple task proved to be rather difficult.

The first step of this process is the preparation of silicon dioxide wafers for graphene deposition. Using a diamond pen, the wafer was cleaved into smaller samples and treated with a five-minute acetone sonication. After an isopropyl alcohols rinse and dried with compressed air, the wafer was ready for any other alterations to maximize graphene production. Etching layers of oxide from the wafer was attempted using a mixture of hydrochloric acid and hydrogen peroxide, which only made it more difficult to optically detect the graphene.

Next, multiple techniques were tried to deposit pieces of graphene onto the substrate. The following is a list of rather unsuccessful techniques; gentle to forceful direct rubbing of graphite, sandwiching graphite between two pieces of substrate, liquid deposition in acetone, heating the sample and cleaving the graphite to expose a fresh atomic layer of graphite. Finally, a technique was used that was seen from Manchester University that uses scotch tape.(5) Taking a single piece of graphite and placing it on the scotch tape allowed the one piece to be multiplied into many pieces in close proximity. This made it more probable to find thin pieces of graphite on the substrate where graphene was usually found.

The majority of the research time was spent on either optical or atomic force microscopy. Scanning a slide using optical microscopy required at least 20x magnification to see the thinner and smaller pieces of possible graphene. Once a point of interest was identified, the magnification was taken up to 100x and a picture was taken using a microscope camera. Finally, another picture was taken using only a 4x magnification for a reference to later find the POI on the atomic force microscope. The atomic force microscope used a tapping technique that oscillated its silicon cantilever at the resonant frequency that was driven to the substrate. Repelled by the van der Waals force, the tip never actually hits the sample. A laser is reflected off the back of the cantilever into a photodector that records height data.

Many samples were created and scanned without finding single layer graphene until sample 080701(1)csf. The particular sample had multiple POI's of varied thickness with one POI that could possibly be a single layer. This sample was a perfect candidate for a new optical technique that we wanted to try using fluorescence microscopy and colloidal gold. The thought was that the nano-particles of gold would absorb a specific wavelength of light from the fluorescence microscope and emit a longer wavelength of light depending on what proximity it had to graphene and how many layers it consisted of. This would give us a different and possibly a more efficient way of detecting a single atomic layer without having to wait long periods of time for the atomic force microscope to scan. After refining techniques to deposit the gold colloid on the substrate, gold was deposited onto sample 080701(1)csf.

Figure 1 shows the possible single layer of graphene before the gold while figure 2 shows the POI after. The technique that worked the best to deposit the gold evenly was to spin the sample on a turntable between 100 and 200 rotations per minute and dropping the gold onto the substrate. Figure 2 shows that doing this will affect the integrity of the sample as one of its corners folded on top of itself. This minor setback led to a thought that would allow me to finally deposit and image graphene. “What if I deposit the gold first and then apply the graphene?”

The first try of this resulted multiple POI’s of extremely small thickness (figure 3) including the first sample of single layer graphene as seen in figure 4. Figure 4 shows two strips of graphene side by side with a 0.8nm height change. The sample on the right shows a large piece with its edge folded over giving a 1.2nm jump with a 0.4nm drop. The first jump from the substrate to the graphene has an extra 0.4nm to it due to the moisture on the substrate. With this discovery, I tried the same technique many times and was able to repeat the process multiple times. Figures 5 and 6 are relatively small scans showing single layers while figures 7, 8 and 9 are larger scans. An interesting feature was seen in these larger scans. Figures 7, 8 and 9 have large white spots around the pieces of graphene. Height analysis shows that these spots are approximately 80nm high, which is the height of the gold nano-particles. Further analysis of other thin POI’s consistently showed these large clumps of gold on or around the layers of graphene. Looking at the portion of the sample with no graphite and graphene showed individual gold particles but no clumps.

The explanation for this is still being tested but it is thought that the gold acts as a source of friction or an anchor to the graphene. Figures 10 and 11 show gold on the substrate by itself and clumps around graphene, respectively. The thought is that the gold particles are acting as friction to the graphite being dragged along the substrate. The gold is shifting around underneath the graphite and clumping together to form larger pieces. These large pieces finally have enough surface area and mass to attach to the substrate and anchor down the graphene pieces, stripping them away from the large graphite pieces. Performing the same steps side by side with a sample with gold and without gold has repeatedly produced the same results.

Future research to be conducted with this graphene includes using a fluorescence microscope to see if, in fact, the gold’s intended purposes helps to not only deposit but image graphene. A recent trial in which moisture has been controlled has initially shown promise in size of pieces found. Devices are being planned for larger pieces of graphene and growth of vanadium dioxide nanowires on top of graphene has begun.

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