Fabrication of Graphene Structures Using an Atomic Force Microscope

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Abstract:
Graphene has been theoretically and experimentally shown to display exceptional thermal, electrical and mechanical properties, which could potentially revolutionize modern electromechanical devices. Despite the possibilities, the capabilities of this two-dimensional (2-D) crystal have yet to be harnessed due to limitations on fabrication techniques and large-scale manufacturing processes. To address these limitations, we investigated an atomic force microscope (AFM) technique, known as anodic oxidation, to etch graphene. This technique achieved graphene patterning on a sub-100 nm scale at a fraction of the time and cost of other methods. Line-widths of the graphene etches were roughly 50 nm. Graphene Van Der Pauw structures and nanoribbon devices will be fabricated on top of 300 nm silicon nitride (SiN) membranes. Chrome/gold electrodes will be evaporated onto the nitride membranes and chemical vapor deposition (CVD)-grown graphene will be transferred on top of them. The graphene will then be patterned into specified dimensions for the Van Der Pauw structures and nanoribbon devices. They will then be electrically characterized and optimized.

Introduction:
Currently there are a limited number of ways to pattern graphene at the nanoscale. The most precise method thus far is electron-beam lithography (EBL) with its finest features in the 10 nm range. Despite the strengths of EBL, it is both extremely costly and time-consuming. A viable alternative is anodic oxidation via an atomic force microscope (AFM) [1]. Anodic oxidation occurs by applying a voltage between the tip and substrate in the presence of water. With graphene on the substrate surface accompanied by a water meniscus, an electrochemical reaction is induced as shown in Figure 1. This reaction causes the graphene to locally oxidize and results in two different scenarios: an etching away of the graphene at sample voltages above 6V and a buildup of reaction products at voltages below 6V. This AFM technique has been established with graphite [2], but has not yet been fully developed with graphene.

This technique is promising for a number of reasons. The sample requires no preparation before etching, unlike EBL, thus there would be no added impurities introduced, such as photoresist. The technique is also versatile; it can be controlled in real-time using programming software. Furthermore, it is cost-effective and efficient using almost the same amount of power and time required to operate the AFM by itself.

Experimental Methods:
Graphene etching was first achieved on a sample of graphene on silicon dioxide (SiO2). Humidity of the room was routinely checked to be above 30%. This was above the threshold for a water meniscus to form and facilitate the electrochemical reaction. The etch process consisted of imaging a specific area, writing a program for the etching parameters and subsequently imaging the same area. The anodic oxidation hardware and AFM tip translation was controlled using a C++ program. A bias of -7V was applied.

Figure 1: Schematic of anodic oxidation using an AFM.
between the tip and substrate for etching. The tip z-depth into the surface was set to -40 nm in order to ensure contact between the tip and surface.

An 800 nm line was successfully etched into multi-layer graphene with a depth of about 2 nm as shown in Figure 2. A box etch was also successfully etched into multi-layer graphene with a depth of 3 nm as seen in Figure 3. Note the accumulations along the etch lines. These are believed to be carbon-based products from the reaction. There was also a tip wear dependence to the etching such that as the tip radius became larger, the etch width also increased proportionally.

In order to fully display the capabilities of this graphene etching technique, Van Der Pauw structures and graphene nanoribbon devices were made on top of silicon nitride (Si₃N₄) membranes. Membranes were used for optical transparency and future piezoresistance measurements. The membranes were made by depositing 300 nm of Si₃N₄ on both sides of the Si wafer using low-pressure chemical vapor deposition. The backside nitride was then patterned using photolithography and subsequently plasma etched using CHF₃/O₂. With the nitride layer acting as a mask, the Si was then etched using potassium hydroxide (KOH), thus creating the nitride membranes on the front side. Electrodes consisting of an 8 nm chrome adhesion layer followed by 40 nm of gold were then evaporated onto the membranes. Graphene was grown on top of a copper foil using CVD and then coated with a transfer layer of poly(methyl methacrylate) (PMMA) on top. The copper was then etched away in ferric chloride and the remaining graphene was transferred onto the electrodes and membranes (Figure 4).

**Results and Conclusion:**

While graphene was successfully etched on the SiO₂ substrate, the Si₃N₄ membranes were not so cooperative. The failure to etch was believed to be attributed to several factors.

First, because the membranes were suspended, the voltage between the tip and substrate was indirect, and would result in a non-localized electric field. This could be resolved by applying the voltage between an electrode and the tip, thus isolating the graphene. Another problem may have been the z-depth to which the tip was pushed into the surface. If it was pushed too far, the water meniscus may have been pushed aside, thus suppressing the reaction. There is also a chance that the parameters, such as the meniscus layer and mechanical control of the AFM, were not being controlled to the precision needed at the nanoscale. These parameters become critical factors for a controlled etch, yet may not be precise at such a small scale.

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**References:**
