Fabrication of Graphene Microelectrodes

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Primary CNF Tools Used: Anatech resist strip, Nikon L200 eclipse microscope, Heidelberg mask writer DWL2000, ABM contact aligner, SC4500 odd-hour evaporator, YES vapor prime oven

Abstract:

We present a method of graphene microelectrode fabrication, which we designed to be able to study the electrochemical properties and applicability of graphene in energy storage, sensing, and electrocatalysis. The fabrication scheme consists of mechanical exfoliation of graphene/graphite crystals, photolithographic pattering of their surface, and metal deposition of electrical contacts.

Summary of Research:

The electrochemistry of two-dimensional (2D) materials such as graphene has been of significant interest to researchers hoping to apply these materials in energy storage, sensing, and electrocatalysis [1]. However, a limited understanding of the fundamental electrochemical properties of graphene has hindered the recent progress, mostly due to lack of well-defined single-crystal graphene samples. Our aim was to fabricate microscale opening within an insulating layer of a polymer in order to study the electrochemical properties of single-crystal graphene/graphite microelectrodes. To that end, we exfoliated bulk graphite onto an insulating substrate and used polymer-based photolithography and metal deposition to create an electrical contact to graphene/graphite and to fabricate the microelectrode opening over the material.

First step in the fabrication process is the mechanical exfoliation of bulk graphite onto anoxidized silicon wafer (SiO_2/Si). The wafers are sonicated in acetone and isopropanol (IPA) in order to remove surface contamination. To maximize the adhesion between the graphite and the wafer, the latter is cleaned by plasma ashing in the Anatech resist strip (at 900 W for 5 min), immediately prior to the graphite exfoliation. The tape use for exfoliation is peeled away, leaving some graphite/graphene crystals on the wafer surface. Examination under the Nikon L200 eclipse microscope reveals crystal of different thickness, readily identified by their optical contrast, as shown in Figure 1.

We then designed and wrote a quartz/chrome photomask (courtesy of Alejandro J. Cortese, McEuen group) using the Heidelberg mask writer DWL2000, to be used with our two-step photolithographic process. Poly(methyl methacrylate) (PMMA) (950K 4% in anisole) was used as the photoresist polymer material for both steps, using the 220 nm mirror, 60 min exposure, and methylisobutyl ketone/IPA (1:3) developer. First, the mask was manually aligned to a selected graphene/graphite crystal and exposed using the ABM contact aligner. This was done in a way such that a window in the PMMA was created, exposing a small portion of the crystal as shown in Figure 2.

Next, the SC4500 odd-hour evaporator was used to deposit a layer of 7 nm Cr and 50 nm Au. The PMMA and top-surface Au/Crwere then removed by a lift-off procedure in acetone (assisted by a methyl methacrylate undercut layer). This resulted in the exposed portion of the crystal in contact with the Au/Cr layer, as shown in Figure 3.

In the second photolithographic step, another PMMA layer was used to cover the entire wafer, another pattern on the mask was aligned to the alignment marks from the previous metal deposition step and exposed using the ABM contact aligner. This resulted in a microelectrode disk opening in the PMMA, exposing the graphene/graphite surface in the final device shown in Figure 4. We then contacted the Au layer to metal wire and erected

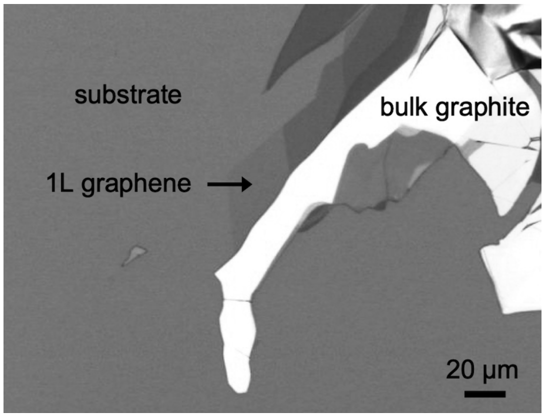

Figure 1: Optical image of graphene/graphite crystals exfoliated on 290 nm SiO_2/Si substrate.

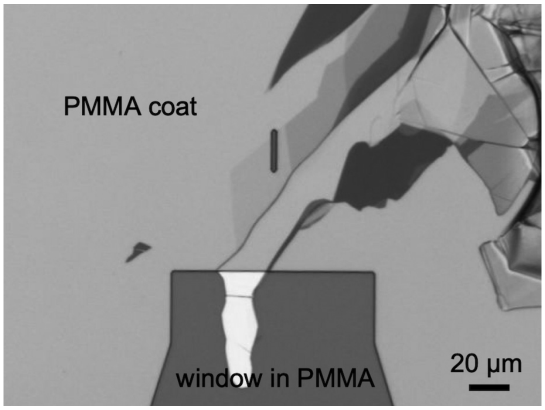

Figure 2: Optical image showing the first photolithographic step with a window in the PMMA exposing apart of the graphite crystal.

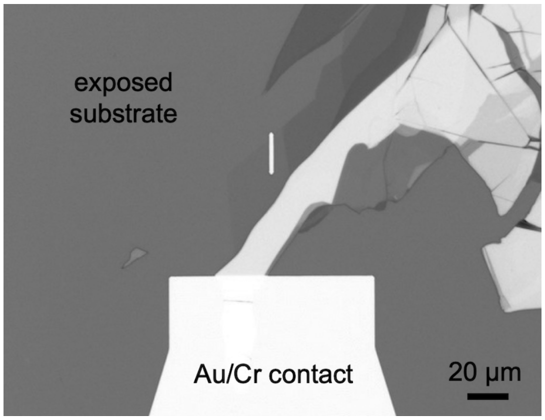

Figure 3: Optical image showing the deposited Au/Cr layer contacting the graphite crystal.

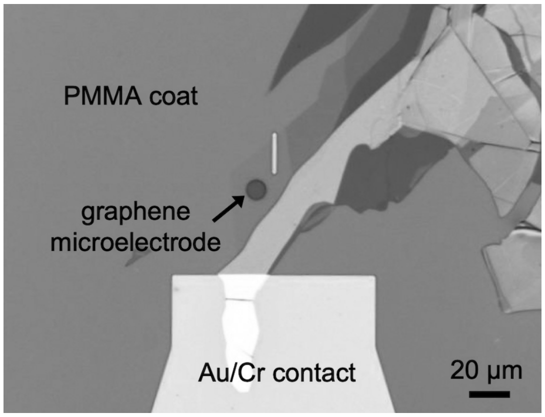

Figure 4: Optical image showing the final device with a 10 µm diameter opening in PMMA exposing a monolayer graphene crystal microelectrode.

an electrochemical cell around this opening made of a several-mm thick polydimethylsiloxane (PDMS), which has previously been set over a silicon wafer surface primed with hexamethyldisilazane using the YES Vapor Prime Oven. The PDMS "pool" has been filled with the liquid solution of interest in order to carry out the electrochemical experiments.

To date, we have not been able to achieve satisfying electrochemical behavior of our devices. Specifically, we either observed no current upon application of voltage or current-voltage characteristics significantly deviating from the behavior expected for the device geometry. We suspect that there are several factors contribute to this discrepancy, namely contamination of the microelectrode from the photolithographic process and either pinholes in PMMA or poor adhesion between the PMMA and the SiO_2/Si substrate, resulting in the liquid "creeping" between the two.

In summary, we succeeded in designing a fabrication scheme, which can produce graphene/graphite electrodes of diameters between 5-100 µm. We currently work towards resolving the aforementioned issues affecting the electrochemical measurement of these devices. We envisage that once these technical obstacles are resolved, we will able to study some of the fundamental relationships, namely the effect of the electric field upon the electron transfer rate between a graphene electrode and a redox molecule in solution. Such fundamental insights will facilitate exploration of graphene and other 2D materials in the electrochemical energy storage/ conversion, sensing, and electrocatalysis.

References:

[1] Velick., M. and Toth, P. S. From Two-Dimensional Materials to Their Heterostructures: An Electrochemist's Perspective. Appl. Mater. Today 2017, 8, 68-103.