Tip-based Precise, Repeatable Etching of Highly Ordered Pyrolytic Graphite

Norimasa Yoshimizu, Bryan Hicks, Amit Lal, and Clifford R. Pollock
School of Electrical and Computer Engineering, Cornell University, Ithaca NY, 14853

This paper describes precise and numerous etching of highly ordered pyrolytic graphite (HOPG) by an atomic force microscope. The current interest in graphene and graphite devices includes sensors and field effect transistors [1]. The latter can be fabricated by generating a band gap in a nanoribbon, but the band gap is affected by single atomic changes in width. Realizing predictable transistor behavior will require precision nanofabrication. Towards this goal, we have studied the chemistry behind graphite etching with a scanning probe and demonstrated precise, repeatable nanofabrication of graphitic structures using an atomic force microscope (AFM) with 10% and 12% precision of 20 nm deep and 32 nm diameter etch holes.

HOPG patterning is accomplished by an electrochemical etch in an AFM. Silicon probes with a Pt thin film coating are used as Pt is conductive, chemically inert, and is a catalyst for carbon corrosion. When an atomic force microscope probe tip approaches the carbon surface, the atmospheric moisture forms a meniscus between the tip and the surface as evident in the hysteresis of the tip displacement curve. Additionally, thermal control is seen to affect the meniscus width which changes the feature size [2]. The meniscus can form consistently even though both HOPG and Pt are hydrophobic. With the tip grounded, a positive voltage is applied to the sample. This causes an electrochemical etch [3] which removes carbon as carbon dioxide, $C + 2\,H_2O \rightleftarrows 4H^+ + 4e^- + CO_2$. The reverse direction is essentially irreversible, and it is typically observed that the hydrogen ions and free electrons in the reaction immediately recombine without being measured as current. Therefore, AFM nanofabrication of HOPG is a non-thermal, electrochemical etching of the surface carbons.

At negative sample biases, it is theoretically possible to etch the HOPG as well, as $CH_4 \rightleftarrows C + 4H^+ + 4e^-$. However, the assembly of the reactants with carbon does not occur and etching is not observed at a negative sample bias. Instead, a negative sample bias is used to intermittently clean the scanning probe tip. The etching process at positive sample bias causes carbon to deposit to the tip, which is the anode in the electrochemical reaction. This is observed by scanning electron microscopy and energy dispersive x-ray spectroscopy to identify the carbon. At negative sample bias, the HOPG is not etched and instead will remove the carbon from the tip. Intermittently cleaning the tip maintains good imaging and lithographic resolution.

To enable precise, numerous etching of HOPG we implemented a digital feedback control loop of the AFM during the etching process to correct for unpredictability of the tip-substrate gap and the etching voltage (Fig. 1). The control loop measures the height of the tip and controls the applied sample bias in response. Before each feature is written, the control loop measures the flat topology of the HOPG as measured by the piezoelectric actuator which moves the AFM tip. When etching lines, for example, the heights of the endpoints are measured and the topology is interpolated. Knowing the initial topology, the electrochemical etching is initiated by applying a positive sample bias, V_H. As the HOPG is etched and the tip moves down through the carbon, the feedback loop begins to reduce the applied sample bias down to V_L just before the desired etch depth is reached. The high initial bias initiates the etching process and proceeds quickly to etch the desired feature, but the low finishing bias generates a smooth, size-controlled feature.

A large 10 by 10 array of holes was etched into HOPG to demonstrate precise, repeatable etching (Fig. 2). The feedback loop was set to a depth of 20 nm. After etching, the array of holes was imaged in the AFM and the resulting distribution of etch times, etch diameters, and etch depths (Fig. 3). The array shows etch times of 20±6 seconds, diameters of 32±4 nm, and depths of 20±2 nm. Note the large variation in etch times for the same resulting etch dimensions.

Figure 4 shows nanofabrication of more complex patterns, including a line and its three dimensional profile, hand-drawn lettering, and a heterogeneous set of lines of two different lengths.

[1] Geim, A. K., Novoselov, K. S., "The rise of graphene," Nat. Mater. 6 pp 183-191 2007
[2] Jang, J., Schatz, G. C., Ratner, M. A., "Liquid meniscus condensation in dip-pen nanolithography," J. Chem. Phys. 116 pp 3875-3886 2002
[3] Pourbaix, M., "Atlas of electrochemical equilibria in aqueous solutions," National Association of Corrosion Engineers New York, pp 449-457 1974

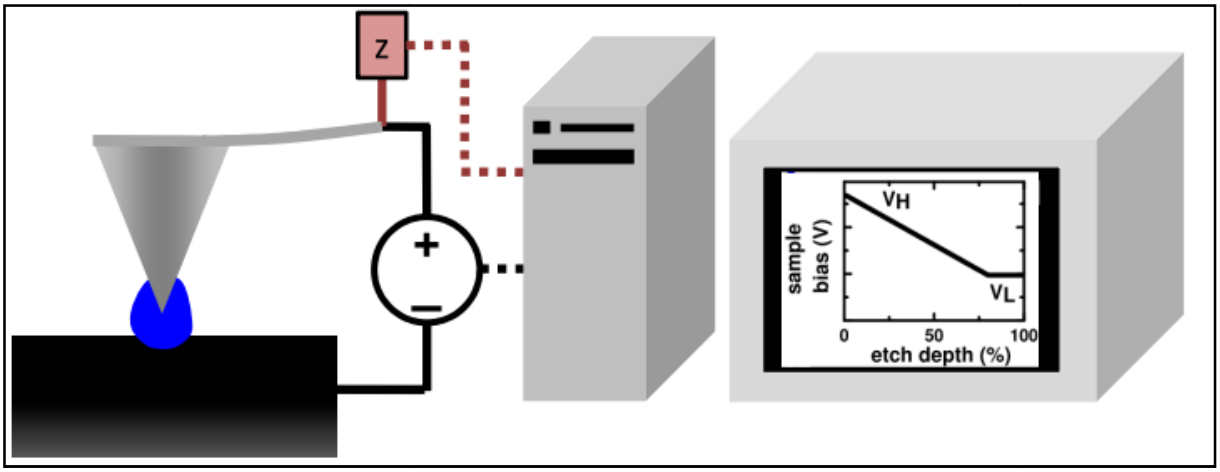


Figure 1 Schematic of precision and numerous nanofabrication of HOPG in an AFM by electrochemical etching. Feedback controls applied bias as a function of etching depth. Small graph shows sample bias – etch depth control curve: high voltage initiates the etch and low voltage finishes with a controlled, smooth etch.

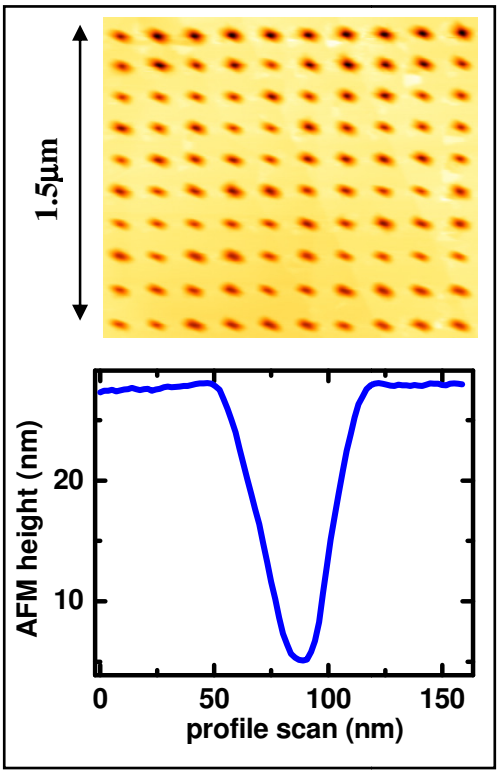


Figure 2 Etching of ten by ten array of 20 nm deep holes in HOPG, with a typical profile.

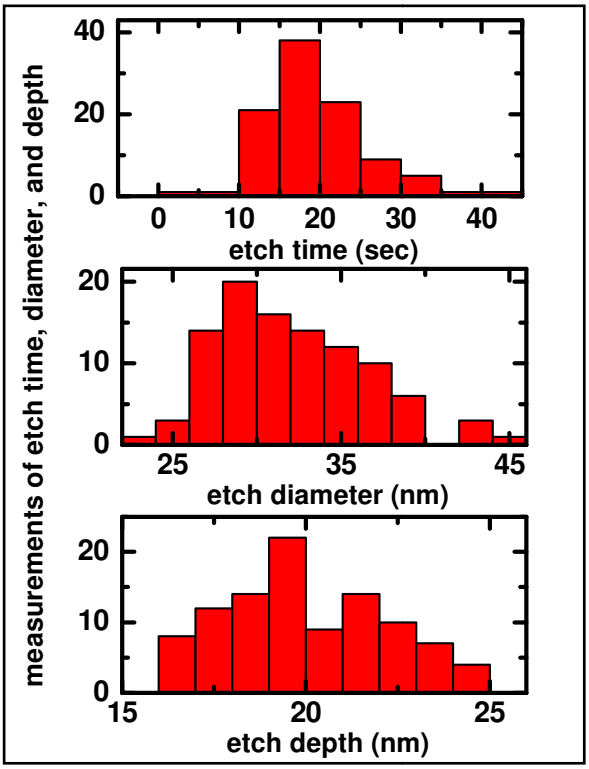
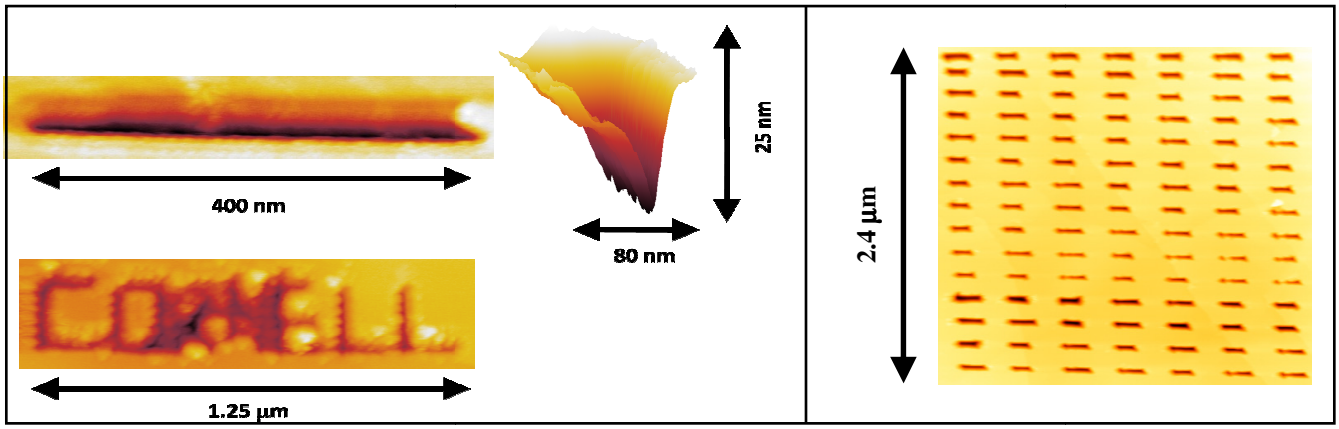


Figure 3 Statistical distributions of hole array yielding 32±4 nm diameters, 20±2 nanometer depths, and 20±6 second total etch times.



Figures 4 In addition to fabricating simple holes, other features have been made by electrochemical etching of HOPG. Lines and other more complicated structures can be fabricated by etching adjacent holes. AFM images show a line, letter writing, and a heterogeneous set of lines.