Mechanistic investigations of nanometer-scale lithography at liquid-covered graphite surfaces

Reginald M. Penner, Michael J. Heben, and Nathan S. Lewis
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Calvin F. Quate
Edward Ginzton Laboratory, Department of Applied Physics, Stanford University, Stanford, California 94305

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Pulse-induced nanometer-scale lithography has been performed on graphite surfaces that were in contact with pure water or other organic liquids. Very reproducible control over the pit diameter was observed in aqueous solutions, and a well-defined voltage threshold (4.0 ± 0.2 V) was also apparent. Near the threshold voltage, 7 Å diameter × 2 Å high protrusions were formed, while larger initial pulse voltages resulted in pits of diameter > 20 Å.

Recently, atomic and molecular scale features have been produced on surfaces using scanning tunneling microscopy (STM) methods. At room temperature, the smallest permanent lithographic process reported to date involves the formation of ~40 Å-diam pits on a highly ordered pyrolytic graphite (HOPG) surface. These pits were formed by the application of 3–8 V pulses of 10–100 µs duration, while within tunneling distances. Although a substantial fraction of the STM tips successfully generated hundreds of uniform pits when subjected to constant amplitude and constant duration bias pulses, the pulse threshold at which the smallest features were observed varied substantially from tip to tip. Additionally, the lithography process was observed to require a humid atmosphere and to exhibit daily fluctuations in pulse bias versus pit size. In order to elucidate the chemistry of this process, we have performed STM lithography studies of HOPG surfaces in contact with water and other organic liquids. For HOPG in H2O(l), we have observed that a voltage threshold (4.0 ± 0.2 V) was also apparent. Near the threshold voltage, 7 Å diameter × 2 Å high protrusions from the surface by 2 Å. Larger voltage pulses yielded pits of diameter > 20 Å.

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Cross-sections of HOPG

FIG. 1. STM images of lithographically modified HOPG in pure water. All images show derivative mode data obtained at a bias of —100 mV, a fast raster frequency (x direction) of 10 Hz, and a slow raster frequency (y direction) of 0.025 Hz. (a) Domed feature produced at HOPG in pure water using a —4.0 V × 12 s bias pulse. Image window is 80 × 80 Å. (b) Large pit (diameter ≈ 80 Å) produced at HOPG in pure water using a —4.5 V × 20 ps pulse. Image window is 400 × 400 Å. (c) Cross sections of the features in (a) and (b) above. The smaller scan line with the positive vertical displacement corresponds to the feature of (a); the other trace refers to the feature depicted in (b).

probability) were stable to imaging at biases as high as ±500 mV for periods of >1 h under the H₂O(l) ambient.

The features in Fig. 1(a) were only formed on graphite surfaces that were in contact with liquid H₂O, and only with pulses near the observed threshold voltage. Incrementally larger bias pulse amplitudes of $E_p = (4.3 - 4.4)V$ produced pits that were qualitatively identical to those observed for lithography on HOPG in air; the diameter of a typical pit formed with a —4.2 V pulse under H₂O(l) was 40 Å, and its depth was 3 Å. This depth is consistent with the removal of a single graphite layer, as proposed earlier for bias-pulse lithography on HOPG in gaseous ambient. Further increases in the bias pulse amplitude resulted in monotonic increases in the dimensions of the resulting pit. As a representative example, Fig. 1(b) shows a derivative mode STM image of an 80-Å-diam pit that was generated with a tip bias pulse amplitude of —4.5 V for HOPG in contact with H₂O(l). Note that the darker region now appears first in the right-to-left scan direction of Fig. 1(b), which is the expected signal for a depression in the surface.

The reproducibility of bias-pulse lithography in H₂O(l) improved in two distinct ways relative to the process in an air ambient. The reproducibility of the threshold voltage (i.e., the voltage required to produce the smallest observed features) was observed to be (—4.0±0.2) V in H₂O(l) for a large number of independent experiments with a variety of STM tips. In contrast, experiments in laboratory air exhibited substantial daily variations of as much as 5 V in the pulse threshold, presumably due to variations in the relative humidity. Second, in H₂O(l) the relationship between $E_p$ and the pit (or dome) diameter was very well defined for pulse amplitudes above $E_p$. Fig.

FIG. 2. Statistics for the feature diameter as a function of the bias pulse amplitude for lithography experiments at HOPG in water. Each data point represents 10 trials conducted with several polymer-coated tungsten tips over a seven day interval. Error bars are the calculated 1σ confidence interval for these data. Two additional points not displayed are as follows: $V = 4.40$ V, diameter $= 210 ± 85$ Å; $V = 4.60$ V, diameter $= 505 ± 155$ Å.

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ure 2 shows statistics relating $E_p$ to the feature diameter; these statistics were obtained using 10 polymer-coated tungsten tips that were fabricated and used in STM lithography experiments over the period of a week. The increased reproducibility obtained in H$_2$O(I) underscores the link between the chemistry of the lithography process and the presence of water during the pulse period.

Several different ambients were investigated in order to confirm the suggestion that H$_2$O is required to form etch pits. At graphite surfaces in contact with either dry toluene(l) or dry N$_2$(g), features could not be generated even with pulse amplitudes as large as $\pm$ 10 V. However, introduction of H$_2$O into either of these ambients restored the ability to produce the features represented in Figs. 1(a) and 1(b). These observations are consistent with those of Terashima et al.$^2$ who observed a suppression of pit formation on graphite in 10 mTorr toluene vapor and in dry N$_2$(g) ambients. Reagent grade organic solvents which were not rigorously dried, such as n-octane and mineral oil, behaved qualitatively like an air ambient. In these impure liquids, variations of the threshold voltage of up to several volts were observed, but in all cases lithography was facilitated at $|E_p| < 10$ V. In these ambients, the lithography operation yielded only pits, as was observed for experiments in air ambient.

For graphite surfaces in contact with H$_2$O(l), the observation of small diameter “domes” at the voltage pulse threshold suggests that these features are intermediates in the formation of the pits that are observed at larger voltages in H$_2$O(l) and at all voltages larger than the threshold voltage in humid air. This hypothesis was supported by the observation that in contact with H$_2$O(l), domes could be converted into 30–40 Å diameter pits by application of a subthreshold, 0.2 V pulse. This indicates that the domes are metastable intermediates, and that they can be converted into pits with suitable physical or chemical stimuli. This also suggests that chemical reagents might be able to lead to subnanometer diameter features not observed previously in gaseous ambients, and leads to improved control over pit diameter at larger voltage pulses. Attempts to exploit these reactive features to achieve site-specific, nanometer-scale chemical derivatization of surfaces is under study at present.

In conclusion, we have shown that STM-based lithography of HOPG in contact with H$_2$O(l) is reproducible, leads to subnanometer diameter features not observed previously in gaseous ambients, and leads to improved control over pit diameter at larger voltage pulses. Attempts to exploit these reactive features to achieve site-specific, nanometer-scale chemical derivatization of surfaces is under study at present.

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11. sp$^2$ carbons were positioned above the plane of the “graphite surface” prior to minimization to mimic the steric repulsion presented by an underlying graphite layer.