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Pulse Induced Nanolithography of Graphite in H_2O: A Road to Chemical Linkages to the Surface?

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PULSE INDUCED NANOLITHOGRAPHY OF GRAPHITE IN H_2O: A ROAD TO CHEMICAL LINKAGES TO THE SURFACE?

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ABSTRACT

The effects of tip-sample bias pulses while within tunneling distances have been investigated for graphite surfaces in contact with dry fluids, fluids containing water, and liquid water. In dry ambients, no surface modifications were observed at pulse voltages in excess of ± 10 V. In fluids containing water, bias pulses exceeding a threshold voltage produced pits in the graphite surface, but the threshold voltage exhibited daily fluctuations of as much as 5 V. At the threshold for surface modification, a typical pit was found to have a diameter of approximately 30 Å and was 3 Å in depth. The diameter and depth of the pits increased with pulse amplitude above the observed threshold. In pure water, a reproducible bias pulse threshold of 4.0 ± 0.2 V was observed, and such pulses yielded dome-like features on the surface. The domed features were found to have a diameter of ~ 7 Å and were ~ 1.5 Å high. Bias pulses greater than 4.0 V were found to produce pits of approximately the same diameter as those produced in humid gases. Although little is known at present about the chemical structure of the domed features, their conversion into pits with subsequent bias pulses of only 0.2 V suggests that they are structural intermediates in the pit formation process. This hypothesis implies that the domed features may be vulnerable to chemical attack; consequently, the domes may present a viable route to the localized, designed, chemical functionalization of a graphite surface

INTRODUCTION

Application of a short bias pulse while within tunneling distance of a highly oriented pyrolytic graphite (HOPG) surface in air is known to produce pits in the surface.[1] Using this methodology, Albrecht *et al.*[1] have been able to write characters on graphite surfaces and Mizutani *et al.*[2] have been able to cut 100 Å diameter, single monolayer deep disks from the top layer of the graphite surface. Although both of these experiments are important examples of surface lithography, neither is currently suitable as a first step in the formation of localized *chemical* linkages to graphite surfaces. In our investigations of the chemistry of this lithography process, we have discovered a new type of surface modification which results in the formation of small, metastable domed features on graphite. These features are formed by pulse bias lithography under pure water, and can be subsequently converted into pits by use of a

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sub-threshold voltage pulse. As described below, this process does appear to have potential for the localized chemical functionalization of graphite.

EXPERIMENTAL

All of this work was performed in a scanning tunneling microscope (STM) designed specifically for operation in fluid media. Details of the instrument and data acquisition instrumentation are described in detail elsewhere.[3] STM imaging of surfaces under solution was accomplished using partially insulated tungsten tips with ~2ml of the desired liquid in the quartz base. Tip preparation consisted of electrochemical etching of .020" diameter tungsten wire, followed by insulation of the wire with a poly(alpha-methyl styrene) (30,000g/eq. MW, Aldrich) solution prepared from a 30 w/v% solution of the polymer in CH_2Cl_2. After etching and coating with polymer insulation, a portion of the metal surface was exposed by the application of a +15 V bias to the tip in air.[4]

STM images were obtained in constant current mode with an X scan frequency of 10-20 Hz. Typical imaging was carried out at a bias of -100 mV, with the surface at ground potential. Bias pulses were of 20 μs duration and were generated with a Wavetek model 802 pulse generator, which also served as the DC bias source. Tunneling line traces were obtained in a tip height vs. position mode. Tunneling images typically were obtained in a constant current "derivative" mode, wherein changes in height of the tip were plotted vs. position. The derivative mode images were obtained with the tip scanning the image from right to left, with bright areas indicating tip movement away from the surface and dark areas indicating tip movement toward the surface. The images were mapped into 256 x 256 x 8 bit array with an Arlunya TF5000 Video Image Processor. The video output of this device was ultimately stored on super-VHS tape. Individual images were reproduced by photographing a desired video image on the screen of a 700 line video monitor. The X and Y displacements of the piezo tube were determined from atomic resolution images of HOPG, while the Z displacements were calculated from the manufacturers specifications for the piezo tube, and were confirmed by laser interferometry.

Experiments in pure $N_2(g)$ were performed in a plexiglass glove box that had been purged with dry $N_2(g)$ for 1 hr before imaging was initiated. Rigorously dry toluene was obtained by distillation from CaH_2 in N_2, followed by a second distillation from titanocene immediately prior to imaging. 18 MΩ-cm resistivity water was obtained from a Nanopure water purification system. All other solvents were used as received from the supplier.

RESULTS AND DISCUSSION

Two typical derivative mode images of a smooth graphite surfaces are shown in figure 1. The image on the left is an atomic resolution image of a graphite surface and displays an interatomic spacing of 2.46 Å. The image on the right is of the same area of the surface with the sensitivity of the grey scale reduced to the level used for the imaging of lithographic features produced on the graphite surface. From these two images, it can be seen that the absence of atomic resolution in images of the lithographic features is not due to a lack of instrument sensitivity; rather, the lack of atomic resolution is simply the result of the grey scale of the large features rendering the grey scale of the atomic periodicity below the level of the noise.

Figure 2 displays a derivative mode image, and a line scan, of the cross-section of a pit formed by a 20 μs, - 4.0 V bias pulse applied to HOPG while tunneling in air.

The derivative image (Figure 2, left), obtained from right to left in the X-scan direction, indicates that the height of the tip decreased and then increased as it traversed the lithographic feature. This image was typical of all pits formed at, or just

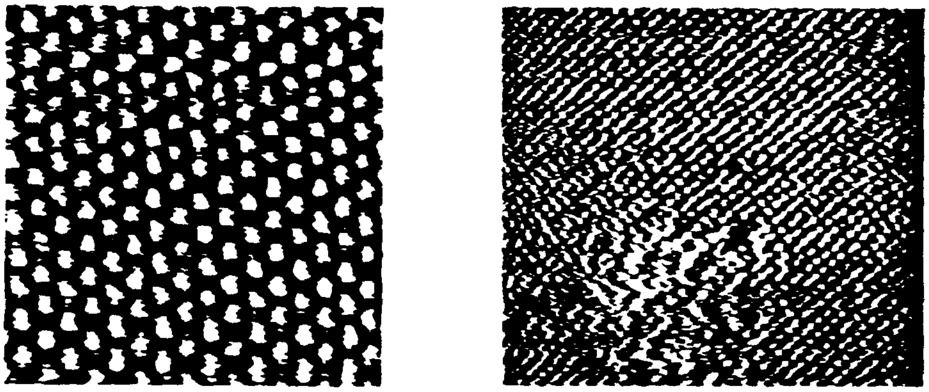

Figure 1. Derivative mode images of the same graphite surface taken in atomic resolution mode, left and with the grey scale adjusted for the imaging of lithographic features, right. In each image the window is 30 Å x 30 Å.

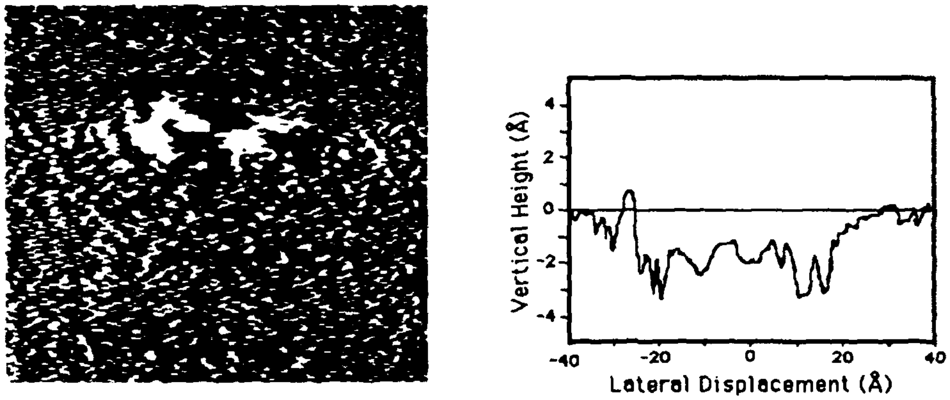

Figure 2. Derivative mode image, left, and a line scan, right, of a pit formed by a 20 μs, -4.0 V bias pulse in air. The image window is 100 Å x 100 Å.

above, the threshold voltage for surface modifications in humid air, wet n-octane and wet mineral oil. The line scan of the pit was also typical of such features, and clearly demonstrates the monolayer depth of these pits. The ability to form pits was independent of the polarity of the bias voltage.

A derivative mode image and several line scans of a domed feature on the surface of HOPG are displayed in Figure 3. The feature was formed by the application of a 20 μs, - 4.0 V bias pulse, while tunneling to the graphite surface in water. The derivative image, again obtained with an X-scan direction from right to left, showed the tip initially rising and then falling, i.e., tracing out a dome-shaped profile relative to the surface plane. These domed features could only be generated when the lithography was performed in water. The line scans verified that this feature was indeed a protrusion, and showed that it was ~ 7 Å in diameter and ~ 1.5 Å high. Like the pits, domes were formed with bias pulses of either polarity. It is important to emphasize that the domed tip profile could occur either from a physical protrusion in the surface topography or from a defect that leads to an increased tunneling probability relative to that of HOPG itself; these two possibilities cannot be distinguished from the constant current tunneling data collected in this study.

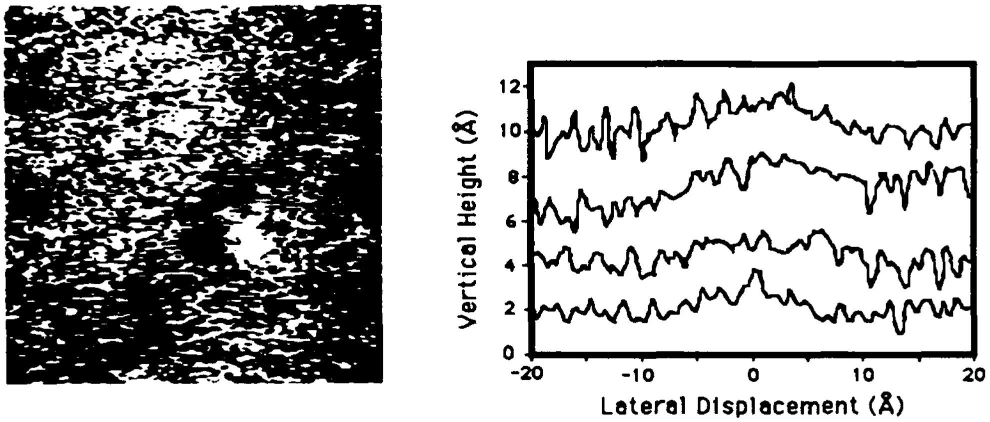

Figure 3. Derivative mode image, left, and several line scans, right, of a dome formed by a 20 μs, -4.0 V bias pulse in water. The image window is 80 Å x 80 Å.

When the lithography was performed in water, the threshold for dome formation was observed to be very reproducible at ± (4.0 ± 0.2) V. These domes were stable to tunneling at biases less than ± 500 mV for periods of greater than one hour, and were verified to be stable in water with no bias for periods of days. However, subsequent bias pulses of only 0.2 V converted the domes into pits; the resulting pits were extremely similar in dimensions to the pit in Figure 1. This observation indicates that the dome can be an intermediate in the pit formation process under certain conditions.

In dry media, the application of bias pulses up to ± 10 V produced no detectable surface modifications on graphite. However, addition of water to either toluene or dry nitrogen restored the ability of bias pulses to produce pits. This observation is in good agreement with the data of Terashima *et al.*[5], who also observed a suppression of pit formation in dry nitrogen and in 10 mTorr of toluene vapor.

Although we have shown that the presence of water is necessary for pulse-bias-induced lithography on graphite, the chemical mechanism of feature formation remains to be identified. The most remarkable results of this study are the polarity independence of pit and dome formation, and ease of the conversion of domes to pits. From these observations, a number of conclusions may be drawn. The first conclusion is that water is essential for the lithographic process to proceed. The second conclusion is that although an electrochemical mechanism is unlikely, a chemical reaction involving water, and perhaps a water plasma, is the most likely mechanism for feature formation. Support for this conclusion can be obtained from the observation that pit and dome formation were independent of the bias-pulse polarity. Also, the observations of Albrecht *et al.*[1] that the process of pit formation occurs on epitaxial gold films in humid air, but is inhibited in vacuum, and their further observations that the process was not a simple mechanical effect of the tip driving into the surface, nor a simple rapid thermal explosion, are consistent with a crucial chemical step in feature formation.

Although Mizes *et al.*[6,7] and Soto[8] have shown that a wide variety of defects in graphite can lead to an increased tunneling probability (and therefore induce a retraction of the tip from the surface in constant current mode), we have chosen to explore the possibility that the lithographic domes do in fact represent protrusions from the surface. To this end, we have carried out energy minimization calculations on a 15 atom carbon cluster in order to simulate the graphite surface. When a single six member ring of carbon atoms was perturbed into an sp^3 hybridization, the resulting strained structure was found to have a 7 Å diameter and to protrude 0.45 Å from the surface. This structure is in reasonable agreement with STM measurements of the dome of HOPG, and consequently, appears to be a reasonable model of this feature. How such a dome might be formed is a matter of pure speculation at this time, and thus we might suggest that it is a result of an attack of the surface by hydrogen radicals liberated from the water by the pulse. Hydrogen radical attack is not without precedent, and it is now widely accepted to be responsible for the growth of diamond films. If this model of the surface is correct, then the strained lattice would be much more vulnerable to chemical attack, and it may represent a viable route to the formation of chemical bonds to the graphite surface. Present research is directed toward testing this hypothesis by introducing a variety of reducing and oxidizing agents into the solution after dome formation, and examining the subsequent chemical reactivity of the domed feature.

CONCLUSIONS

We have investigated the role of water in bias pulse lithography in a variety of gaseous and liquid media, and have found that the process is entirely inhibited by the absence of water. Bias pulse lithography performed in wet gases resulted exclusively in the formation of pits in the surface, and the threshold for pit formation varied dramatically from day to day. However, bias pulse lithography in pure water displayed a reproducible voltage threshold, and resulted in the formation of domes as well as pits. The bias polarity independence of the process in water strongly suggests that the process is not electrochemical in nature. Domes were stable for days to imaging, but could readily be transformed into pits with a sub-threshold bias pulse. The metastability of the domed features suggests that they might potentially provide a convenient route to the local chemical functionalization of graphite surfaces.

REFERENCES

1. T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, C. F. Quate, and D. P. E. Smith, Appl. Phys. Lett. 55, 1727 (1989).
2. W. Mitutani, J. Inukai, and M. Ono, Jap. J. Appl. Phys. 29(5), L815 (1990).
3. M. M Dovek, M. J. Heben, C. A. Lang, N. S. Lewis, and C. F. Quate, Rev. Sci. Instrum. 59, 2333 (1988).
4. M J. Heben, M. M. Dovek, N. S. Lewis, R. M. Penner, and C. F. Quate, J. Microsc. 152, 651 (1988).
5. K. Terashima, M. Kondoh, and T. Yoshida, J. Vac. Sci. Technol. A8, 581 (1990).
6. H. A. Mizes, S. Park, and W. A. Harrison, Phys. Rev. B 36, 4491 (1987).
7. H. A. Mizes, and W. A. Harrison, J. Vac. Sci. Technol., A6 300 (1987).
8. M. R. Soto, Surf. Sci. 225, 190 (1990).

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