A Systematic Study of Graphite Local Oxidation Lithography Parameters Using an Atomic Force Microscope

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We apply nanoscale local oxidation lithography to nanopattern graphite using an Atomic Force Microscope. Systematic relationships between the produced feature size and process parameters such as applied tip voltage, water meniscus length, and tip speed during oxidation were observed. By methodically varying these process parameters, we have found the appropriate working ranges to create features of various sizes based on the oxidation of graphite structures. Feature depths and widths down to 1.2 nm and 55 nm, respectively, were obtained under low relative humidity (<30%) conditions. Optimizing the tip speed during patterning was found to be critical in maintaining the presence of the water meniscus, which was found to break above a speed of 0.10 μm/s. The results are directly applicable to nanopatterning single and bi-layer graphene in order to create advanced nanoelectronic devices.

Keywords: Atomic Force Microscope, Lithography, Graphene, Anodic Oxidation.

1. INTRODUCTION

The Atomic Force Microscope (AFM) is typically used for imaging, but has also been used to pattern various oxidizable materials using local anodic oxidation.¹⁻⁹ In the ambient environment, a water meniscus naturally condenses between the AFM tip and substrate.¹⁰ Applying an electric field to the conductive tip causes the dissociated OH⁻ ion to oxidize the substrate, resulting in an etched pattern. Recently, AFM tip-based local anodic oxidation has been used to pattern graphene.¹¹⁻¹³ However, a systematic study on the relationship between patterning parameters and feature sizes has not yet been reported. If the lithography parameters are understood and well controlled, this technique can potentially be utilized for repeatable sub-25 nm patterning on graphitic materials for emerging nanoelectronics applications such as field-effect transistors made from graphene nanoribbons (GNRs).¹⁴⁻²³ While GNRs and other related nanostructures can be fabricated using conventional e-beam lithography,²⁴ AFM local oxidation, if fully implemented, is an attractive alternative with no resist processing steps or vacuum setting necessary. We have recently applied nanoscale anodic oxidation lithography to carbon nanotubes and showed systematic trends between the produced feature size and the corresponding process parameters, with a minimum feature size of 58 nm.²⁵ Here we apply the AFM local oxidation technique to graphite and describe systematic trends between the applied voltage, water meniscus length, tip speed and the resulting feature size.

2. EXPERIMENTAL PROCEDURES

A Pacific Nanotechnology (NANO-I) AFM was modified with electrical connections between the tip mount and stage to the AFM voltage source (Fig. 1). The substrate was kept grounded while the tip was negatively biased. A few experiments with the substrate at positive voltage and a grounded tip showed similar results. Conductive wear-resistant diamond tips were used for both imaging and oxidation. The AFM imaging error was found to be +/-0.2 nm in the z-direction and +/-0.1 nm in the x-y direction. The experiments were conducted on mechanically exfoliated graphite on conductive silicon. Imaging was conducted in contact mode. The varied parameters were voltage, water meniscus length (hereafter known as setpoint), and tip speed under less than 30% relative humidity.
conditions. Patterns were created by scanning the AFM tip in a line across the graphene at a constant speed and setpoint while continuously applying a constant voltage. Voltage was varied from $-5$ to $-10$ V, setpoint from 0 to 130 nm, and tip speed from 0.03 to 0.1 $\mu$m/s. The feature size (depth and width) of the resulting oxidized lines was measured and analyzed using the Pacific Nanotechnology Nanorule software.

3. RESULTS AND DISCUSSION

3.1. Feature Depth and Width versus Tip-Substrate Distance

The first set of experiments was carried out at a constant tip speed of 0.03 $\mu$m/s and $<30\%$ relative humidity condition. Figure 2 shows systematic trends of the achieved feature depth (Fig. 2(a)) and feature width (Fig. 2(b)) for variation of the setpoint and tip voltage. The observed trends can be explained by the tip-meniscus-substrate interaction. When the tip is raised (lowered), i.e., the setpoint is increased (decreased), the water meniscus becomes stretched (contracted). Thus, its diameter on the graphite substrate and the resulting feature dimension changes accordingly. In addition, the feature size is also decreased with increasing (negative) voltage. A change in applied voltage changes effectively the volume of oxidized carbon, such that an increasing voltage creates smaller features. Thus as both setpoint and voltage increase, we observed a strong decrease in feature size as shown in Figure 2. Experiments conducted at $-7$ V and higher resulted in no observable features, indicating the existence of a voltage threshold under these particular experimental conditions ($<30\%$ humidity, 0–130 nm setpoint, 0.03 $\mu$m/s tip speed). Additionally, at $-8$ V and higher tip-substrate distances ($>90$ nm), no etching of the graphite substrate was observed. Evidently, under these conditions the electric field is too weak to oxidize the graphite.

In Figure 2(a), the observed large variance in feature depth between voltage steps indicates that the electric field is the dominating factor in controlling this dimension. Specifically, it is strongly suggested that a larger electric field dissociates a proportionally large concentration of $OH^-$ ions in the meniscus at the substrate, which in turn oxidizes a larger concentration of carbon atoms. Since the width of the feature is limited by the meniscus diameter, the ions can only etch in the $z$-direction, thus increasing the etch depth with increasing electric field. Varying the setpoint between 0 to 60 nm for each voltage setting has little to no influence on the resulting feature depth. In Figure 2(b), at high setpoints, we noticed a convergence of

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**Fig. 2.** (a) Feature depth dependence on setpoint (i.e., water meniscus length) and voltage. (b) Feature width dependence on setpoint and voltage. In both (a) and (b), a clear correlation is seen between voltage, setpoint and feature size. Note that at setpoints beyond 130 nm, no oxidation occurs. This is attributable to water meniscus breakage during the oxidation scan and, in the future, can be remedied by applying voltage while holding the tip stationary over specific points on the graphite substrate. Experimental conditions: tip speed—0.03 $\mu$m/s, humidity—$<30\%$. The y-axis in (a) is plotted on the log scale.
all three voltage conditions to a feature size range of 50–60 nm. This can be attributed largely to the low humidity condition and AFM tip radius of curvature. At these high setpoints, the meniscus diameter can be approximated as equivalent to the AFM tip diameter, which is 60–70 nm. Thus, the achievable minimum feature widths are constrained to greater than 50 nm as dictated by the size of the AFM tip itself.

The corresponding AFM images of the created nanostructures in graphite are shown in Figures 4(a and b). The AFM scans confirm the relationship between feature size and setpoint and feature size and voltage, respectively. In Figure 4(a), as the tip is raised above the substrate from 35.5 nm to 59.2 nm in increments of 11.8 nm, the expected reduction in feature size is clearly observed. Similarly, in Figure 4(b), as the voltage is varied from $-10$ V to $-8$ V in increments of 1 V, feature size is observed to decrease.

### 3.2. Feature Depth and Width versus Tip Speed

A second set of experiments has been carried out to determine the influence of the tip speed on the feature depth. The data shown in Figure 3 were taken at $-10$ V, 0 nm setpoint and $<30\%$ relative humidity. A general relation between tip speed and feature size is seen—faster speeds tend to correspond to smaller feature sizes. The shorter the time the tip spends at each point, the less oxidation occurs and thus feature size is reduced. An experiment examining the dependence of feature width on tip speed was also performed, but the data showed no clear trend due to limited statistics (not shown). However, Figure 4(c) clearly illustrates the expected relationship between tip speed and feature size. As tip speed was increased from 0.03 to 0.10 $\mu$m/s in increments of 0.04 $\mu$m/s, feature size (width and depth) decreased. Further experiments conducted at tip speeds greater than 0.10 $\mu$m/s did not result in observable features. These results are attributed to the graphite substrate hydrophobicity as well as the low relative humidity. Under these conditions, it is strongly suggested that the graphite repels the water meniscus, resulting in its breakdown at these relatively faster tip speeds.

### 4. CONCLUSIONS

This experimental work on AFM tip-based oxidation lithography performed on graphite has determined systematic relationships between the process parameters voltage, setpoint, tip speed and the resulting feature size. Minimum graphite etched feature depths of 1.2 nm and widths down
to 55 nm, were found at −9 V, 95 nm setpoint and <30% humidity conditions. Further progress can be achieved by patterning at higher setpoints, using smaller AFM tip sizes and by introducing a fine environmental control of the AFM system, which will provide insights on the effect of humidity on feature size. The systematic study presented here on graphite is directly applicable to graphene. Thus, forthcoming experiments will utilize the observed trends to pattern single and bi-layer graphene into GNRs and other nanostructures in order to fabricate nanoelectronic devices and study their electron transport properties.

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References and Notes

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