Effects of moisture on Fowler–Nordheim characterization of thin silicon-oxide films

Charles A. Peterson,[a] Richard K. Workman, and Dror Sarid[b]
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

Bert Vermeire and Harold G. Parks
Electrical and Computer Engineering Department, University of Arizona, Tucson, Arizona 85721

Dennis Adderton and Peter Maivald
Digital Instruments, Santa Barbara, California 93117

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A conducting-tip atomic force microscope was used as a Fowler–Nordheim characterization tool of thin silicon oxides. The system was operated under a controlled environment using novel cantilevers fabricated from platinum/iridium wire and nickel foil. With this tool, humidity-dependent field-induced oxidation of the samples and variations in the tunneling current due to uneven water layer coverage were investigated. It is shown that baking the samples and characterizing them under a dry environment alleviates problems arising from the humid environment. © *1999 American Vacuum Society.* [S0734-2101(99)05705-X]

I. INTRODUCTION

As the size of semiconductor devices shrinks, the demand for tighter control on defects in metal–oxide–semiconductor field effect transistor (MOSFET) dielectrics rises. According to the Semiconductor Industry Association's *Technology Roadmap*, the ability to analyze ''localized gate oxide and field oxide defects'' (e.g., ionic contamination, charging effects) is a process integration need that is not expected to have a solution for the next 10–15 years.[1] Over the past 10 years, various scanned probe techniques emerged as important tools for investigating the local properties of surfaces including scanning tunneling microscopy, atomic force microscopy, and scanning capacitance microscopy.[2] None of these techniques, however, is ideally suited for characterizing localized defects in thin dielectric layers on silicon. Therefore, a conducting tip atomic force microscope (CT-AFM) has recently been developed, where a feedback-controlled voltage is applied between the tip and sample in order to maintain a constant picoamp-level tunneling current in the Fowler–Nordheim (FN) regime while raster scanning the sample.[3–8] The FN current, being dependent on the local thickness and other qualities of the probed dielectric, makes it possible to obtain simultaneous maps of the dielectric's surface topography and thickness or quality at a resolution of at least 8 nm.[3]

Variations of this system have already demonstrated thickness mapping of oxides and nitrides on silicon[3–6,9] and local breakdown strength and carbon contamination of oxides on silicon.[10,11] Figure 1 displays typical simultaneously obtained AFM and FN constant-current tunneling images of a silicon sample covered with a thin layer of silicon oxide. The FN image shows several parallel lines where a lower voltage was required to maintain the constant current, the largest of the lines being 200 nm wide. Assuming that all other oxide qualities are spatially uniform, in the FN regime a constant current requires a constant field, thus variations in the required voltage are easily converted into variations in oxide thickness. Such an analysis of the ''depth'' of this line implies that at that location the oxide was thinner than the average 4.5 nm by 0.5–1 nm. The lack of features on the AFM images indicates that these lines appear at the oxide-silicon interface. These lines may be the result of the presence of scratches on the silicon surface before oxidation.

So far, images such as these have been obtained in an environment where water vapor was allowed to adsorb onto the oxide. The presence of a surface water layer due to a humid environment provides several advantages for FN characterization: (a) The surface water forms a meniscus between the tip and sample,[12] and since this layer is conducting,[13] a good electrical contact is formed. (b) Since the water layer acts to extend the electrical contact out beyond the tip-sample region, the effective tunneling area is increased, providing greater tunneling current at a given field. (c) Since the diameter of the tunneling area defined by the meniscus is much greater than the thickness of the oxide, the field is more uniform and less likely to cause oxide breakdown. Note that the uniformity of the field is also useful for comparisons with FN theory and with standard gate oxide integrity measurements, where the geometry is assumed to be that of a parallel-plate capacitor.

However, it is well known that ambient water vapor, if allowed to contact a freshly oxidized Si surface, will not only adsorb onto the surface but will also diffuse into the SiO_2.[14] Thus despite the previous advantages, Fowler–Nordheim characterization in a humid environment may not be acceptable because of the following reasons: (a) Nonuniform surface coverage by moisture, by increasing the tunneling area, degrades the resolution of the resistivity map. (b) The high fields required for obtaining measurable tunneling currents across a moisture-containing oxide, especially for a nega-

[a]Electronic mail: capeters@physics.arizona.edu
[b]Electronic mail: sarid@sarid.opt.-sci.arizona.edu

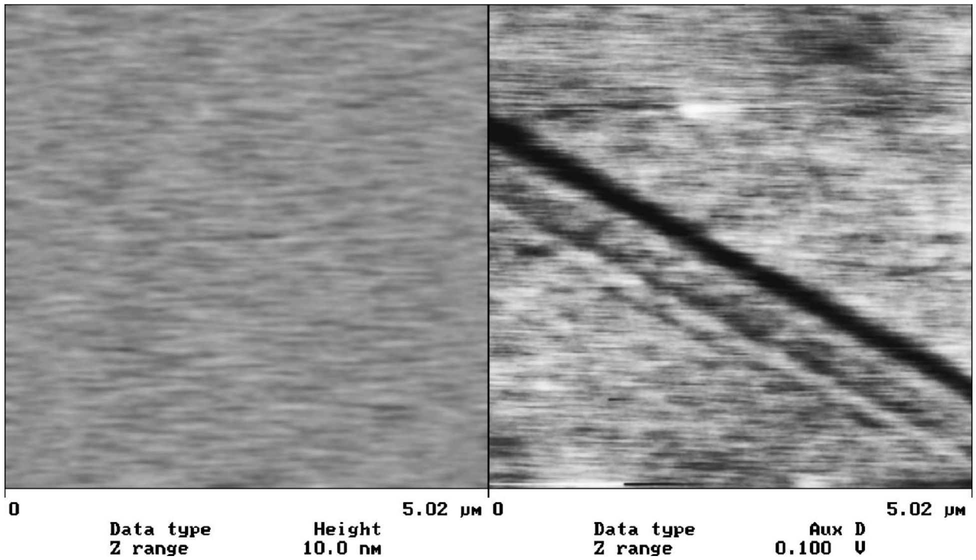

FIG. 1. Simultaneously obtained AFM (left) and FN tunneling (right) images of the sample under investigation. The FN image was obtained by recording the voltage required to maintain 5 pA of tunneling current through the oxide. This image indicates the presence of several parallel lines that do not appear in the corresponding AFM image. This implies that the features are at the oxide–silicon interface.

tively biased gate (tip), will cause local field-induced oxidation (FIO) of the sample.[5,15]

In this article we report on experiments that explore the effects attributed to a wet environment and show that operation on baked samples in a dry environment eliminates these adverse effects, albeit at the expense of having to use higher fields. Also reported is the performance of two novel types of cantilevers, one fabricated from platinum/iridium wire and the other from nickel foil.

II. EXPERIMENT

The experiments reported here were performed using a CT-AFM system based on a modified commercial AFM.[16] The conducting cantilevers consisted of two homemade types. Pt/Ir cantilevers were constructed of platinum/iridium wire[17] and Ni cantilevers were constructed from nickel foil.[18,19] The samples consisted of p-type, 7 Ω cm (100) silicon wafers that were cleaned with SC1-last, forming a thin chemical oxide. The wafers were then thermally oxidized to a thickness of approximately 4.5 nm, as measured by ellipsometry.

The environment of the system was controlled by operating the CT-AFM inside a bell jar. The wet-environment experiments were performed by humidifying the bell jar with a Petri dish containing de-ionized water. The system was allowed to reach a desired relative humidity (RH), after which the dish was removed.[20] Force curves were performed to check for the presence of a thin layer of water on the oxide which will attract the AFM cantilever.[12] The dry-environment experiments were performed after baking the sample at 300 °C for 30 min in a tube furnace with a flow of dry nitrogen to remove water in the oxide. After installing the sample in the system, the bell jar was flushed with ultrahigh-purity nitrogen. Again, force curves were performed to confirm the lack of a surface water layer.

The experiments consisted primarily of performing repeated I-V curves at a given location on the samples, or of scanning the samples while maintaining a constant tunneling current that yields a resistivity map. Specifically, for obtaining most of the I-V curves, the tip was positioned near the upper left-hand corner of a scan area and 10 successive I-V curves were taken, 20 s apart. A preamplifier with less than 0.5 pA noise over a bandwidth of 4 kHz was used to measure the current, the voltage was ramped in 25 mV increments, and the sample was illuminated to minimize any voltage drop in the silicon. The tip was then moved 10 μm to the upper right-hand corner and 10 more curves taken. This procedure was repeated for the lower left- and right-hand corners. In order to interpret the variations in the I-V curves in subsequent experiments, several sets of I-V curves were obtained, each at least 10 μm apart, in both bias directions and in both wet and dry environments to determine the form of a typical curve under each condition. The tip was cleaned[17] prior to each experiment to remove contaminants that may have accumulated during operation of the system, particularly when breakdown of the oxide occurred.

Figure 2 displays two sets of typical curves obtained in a wet environment with a Pt/Ir tip for positive (set A) and negative (set B) gate biases. Within each set, the curves are seen to shift towards a higher applied bias, eventually converging to a single curve. According to Dumin *et al.*,[21] this shift is characteristic of electron trapping in the oxide. Although not able to be derived from this work, Dumin concludes that this trapping occurs uniformly throughout the oxide. Ideally, the initial curves are a good representation of the oxide properties. However, for the large current densities required in this experiment, significant charge is trapped while the curve is taken, thus causing the curve to become distorted. The trapping, however, eventually saturates and later curves taken in the same location overlap reproducibly with

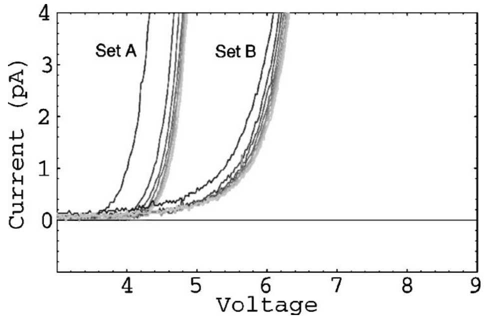

FIG. 2. Typical I-V curves for tunneling on a 4.5 nm thick oxide in a wet environment with (A) positive and (B) negative gate biases. The slight shifts towards higher voltages within each set are due to charge trapping.

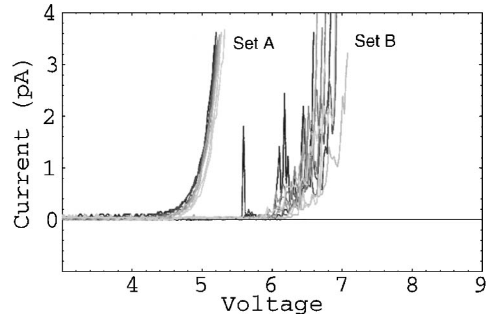

FIG. 3. Typical I-V curves for tunneling on a baked, 4.5 nm thick oxide in a dry environment with (set A) positive and (set B) negative gate biases. The higher biases required for tunneling from the tip and the lack of a tip-sample water meniscus causes localized oxide breakdown leading to spiking in the negative curve. The positive gate bias curve in the dry environment displays the same shift towards requiring higher voltages in subsequent scans at the same location as both curves in the wet environment.

a shift in voltage from the initial curve. Since only the later curves were stable and reproducible, the initial curves have been removed from subsequent plots for the sake of clarity.

In the wet environment, positive gate bias curves required approximately 4.3–4.7 V to reach a tunneling current of 3 pA, while negative gate bias curves required approximately 6.1–7.2 V to reach the same current. The observed voltage difference was the reverse of what would be expected due to the formation of a depletion layer in p-type silicon under a positive gate bias. This difference in voltage is explained by the difference in barrier heights for electron emission into the oxide (3.1 eV for positive gate bias and 4.6 and 4.2 eV for negative gate bias with 90%/10% Pt/Ir and Ni tips, respectively[22]). Deviations from these bias ranges can be attributed to the presence of an insulating material between the tip and sample as a result of either surface contamination or imperfect tip cleaning techniques. The ranges in the biases are due to charge trapping and oxide thickness variations that form the basis of the FN characterization system. It was found that despite a 0.4 eV difference in the work functions, curves obtained with a Ni tip were indistinguishable from those obtained with a Pt/Ir tip. This may be a result of hole tunneling which may become a concern when the barrier to electron injection is greater than about 4 eV.[23]

Figure 3 shows the results of the same experiment now performed in a dry environment on a baked sample with a Ni tip. Here again the curves obtained with a Pt/Ir tip were indistinguishable from those obtained with the Ni tip. It was observed that I-V curves performed with a positively biased gate (set A) required approximately 4.8–5.3 V to reach the tunneling current of 3 pA. However, I-V curves performed with a negatively biased gate (set B) could not be obtained due to the presence of spikes in the curve. A dirty tip as the cause was ruled out by subsequently performing a set of positive gate bias I-V curves, thus confirming good contact. The possibility of air breakdown near the tip as a cause of spiking was ruled out due to the small pressure-gap distance product ($pd = 7.6\times10^{-5}$ cm Torr $\ll 10^{-3}$).[24] Because negative gate bias curves could not be obtained, the experiments used positive gate biases unless otherwise noted.

It is believed that the spiking indicates oxide breakdown due to a combination of the higher biases required to tunnel from the metal and the lack of a water meniscus at the tip-sample contact. Figure 4 is a calculated plot of the electric field intensity between the tip and sample with and without the presence of a water meniscus. In this model, the oxide was chosen to be 5 nm thick, the adsorbed water layer was treated as a dielectric and was 2 nm thick, and the meniscus had a Kelvin radius of 2 nm.[12] A bias of 7.5 V was applied between the tip and sample and no band-bending effects were included. The fields were calculated numerically by solving Poisson's equation assuming no currents. More intense fields are shown with darker shading where black indicates a field of 20 MV/cm. To inject a measurable current

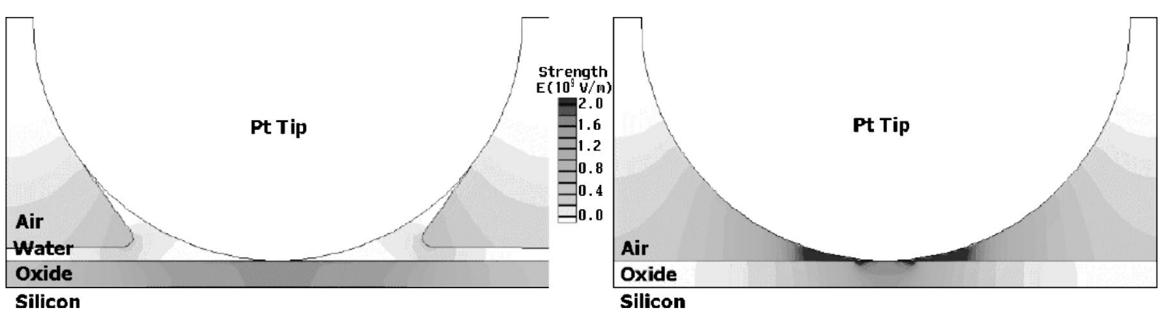

FIG. 4. Plots of the electric field intensity in and around a 5 nm thick oxide when a 7.5 V bias is applied: (a) with a tip-sample water meniscus and (b) without one. Stronger fields are shown with darker shading where black is a field of 20 MV/cm. When the water meniscus is present, the electric field intensity is highly uniform compared to the ''no meniscus'' case.

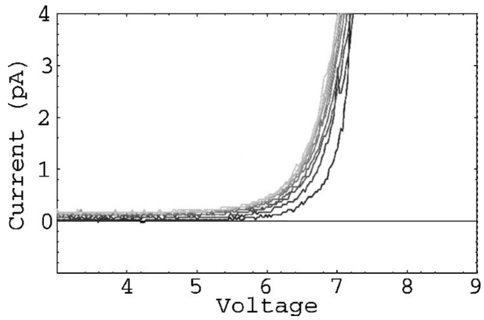

FIG. 5. A set of 10 I-V curves obtained with a negative gate bias on a baked sample in near 100% relative humidity. As the tip-sample water meniscus forms, the effective contact area grows and the curve shifts towards a lower voltage.

(greater than 0.1 pA) through the metal-oxide barrier (4.2 eV for Ni-SiO_2) with such a small contact area, the required fields are nearly enough to break down the oxide. In a wet environment, where the meniscus exists, the fields between the tip and sample behave much like a parallel-plate capacitor and are consequently quite uniform. When the meniscus is not present, the fields become highly nonuniform and intense enough near the tip to cause breakdown of the oxide which subsequently heals.[25] When the current is injected from the silicon, the barrier is only 3.1 eV, and lower fields are therefore required for a measurable tunneling current. Under these conditions, oxide breakdown and current spiking do not occur even without the water meniscus.

A comparison of the positive gate bias curves of the wet and dry samples indicates a shift of approximately 0.5 V. However, to effectively demonstrate the dependence of the tunneling current on the size of the meniscus, it was necessary to design an experiment where the oxide thickness was constant as the meniscus was varied. Comparing baked and unbaked sample was not possible since this would require placing the tip in a different location that may have a different oxide thickness. However, varying the meniscus could be accomplished by obtaining a set of I-V curves on a baked sample placed in a wet environment (60% RH). In this experiment, the tip and sample were initially dry, with no meniscus present. The high humidity, however, caused the formation of a water meniscus over a period of several minutes. The presence of the meniscus allowed negatively biased gate curves to be taken.

Figure 5 shows the resulting curves. Due to the formation of a meniscus, only very minor spiking was visible in the curves. It was found that the initial curve in the set required a higher bias while subsequent curves shifted to the left, the reverse of what is expected for charging (Fig. 2). This is interpreted as an increase in contact area due to the formation of a water meniscus. Since the observed current is directly proportional to the contact area, a simple scaling of the initial and final curves suggested a threefold increase in tunneling area.

For obtaining tunnel maps such as that shown in Fig. 1, the area of interest on the sample was first scanned without an applied bias to check for topographical homogeneity. The area was then rescanned while applying a bias such that a constant tunneling current of 0.1 pA was maintained, producing images with typically 10 mV root mean square (rms) noise. Finally, the area was reimaged without a bias and with a larger scan size to check for surface modification due to the previous scan.

To demonstrate field-induced oxidation of the sample surface while obtaining tunnel maps in a wet environment (55% RH), a tunnel map of a $1\times1\ \mu m^2$ area was taken while maintaining a 2 pA tunneling current with the bias applied such that the current was injected from the Ni tip (negative gate bias). Then, the sample was imaged at $10\times10\ \mu m^2$ using a conventional AFM to determine the effects of the previous scan. The experiment was repeated with a freshly cleaned tip and by injecting current from the silicon sample (positive gate bias). A similar experiment was carried out on a baked sample in a dry environment.

Field-induced oxidation in a wet environment was evidenced in the $10\times10\ \mu m^2$ image, Fig. 6(a), taken after the 2 pA negative gate bias scan with a Ni tip. An area that has oxidized to a height of 1.8 nm above the surrounding surface is plainly visible, and in accordance with earlier research regarding FIO.[5,15] The $10\times10\ \mu m^2$ image taken after the 2 pA positive gate bias scan, Fig. 6(b), also shows an area of oxidation, with a height of only 0.8 nm above the surrounding surface. The same experiment performed in the dry environment (positive gate bias only) displayed no such oxidation. Note that operation in a dry environment but without baking the sample displayed a small contact area due to the lack of a surface water layer while still allowing oxidation due to absorbed water inside the oxide.

III. DISCUSSION

The results of the reported experiments clearly indicate that Fowler–Nordheim characterization, using a CT-AFM, requires baked samples and a dry environment. This need arises because of the adverse effects encountered while operating in a humid environment: variation in the measured tunneling current and field-induced oxidation of the sample.

To make FN characterization a useful tool, it is necessary that it produces results that are strictly a function of controlled experimental parameters. It was observed in the experiments that during the formation of a water meniscus the I-V curves shifted. This shift in voltage was attributed to the increase in effective contact area with the presence of a tip-sample water meniscus. It is therefore reasonable to assume that while operating in a humid environment on a sample covered by a nonuniform water layer, spatial variations in voltage may be observed that are not a result of oxide features. It is also likely that the increased contact area will reduce lateral resolution. Operation in a dry environment is therefore critical.

Field-induced oxidation of the silicon substrate using a CT-AFM has been discussed over the last several years and various models have been proposed.[26–28] These models assume the presence of a negative gate bias to enhance the transport of hydroxide ions toward the silicon substrate

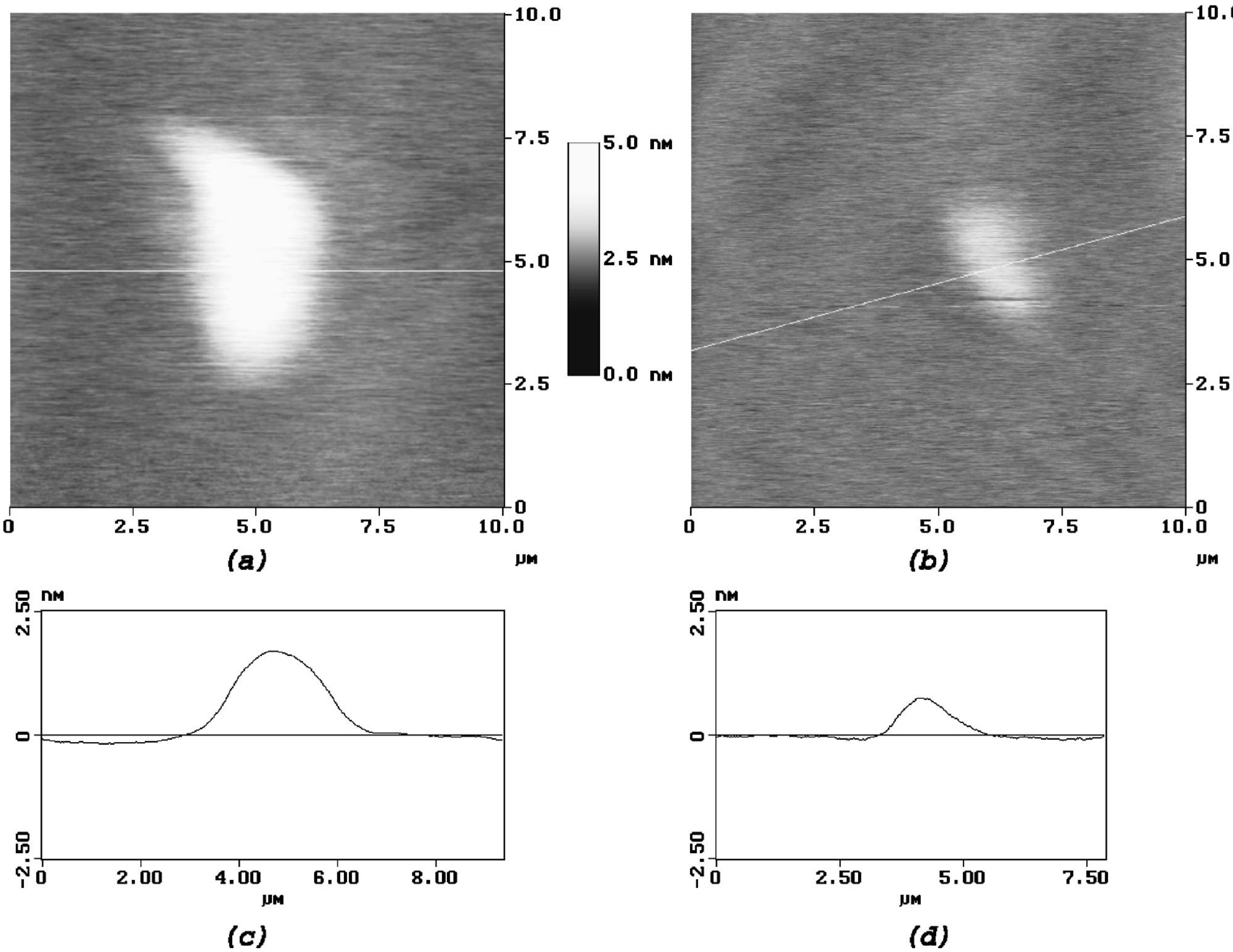

FIG. 6. Contact-mode AFM image of a smaller area where a (a) negative and a (b) positive gate bias, 2 pA current was maintained for tunnel mapping while in 55% relative humidity on a sample that was not baked. Field-induced oxidation of the sample has occurred in both cases. The respective cross sections are shown in (c) and (d).

where oxidation occurs, and are thus in agreement with our experimental results under wet conditions with a negative gate bias. The models suggest that the enhanced transport of ions is linearly proportional to the field strength in contrast to the exponential dependence for Fowler–Nordheim tunneling. Thus, FIO tends to occur over large areas surrounding the tip, while the tunneling is limited to a small area under the tip apex, allowing high resolution images to be obtained. The oblong outline of the feature in Fig. 6, which is much larger than the 1×1 μm^2 scan, is therefore believed to be due to the large-scale tip shape which is known to be asymmetric. Note that the models of FIO fail to explain the oxidation observed with a positive gate bias; however, they do explain the asymmetry in oxide thickness between positive and negative gate biases and that the lack of water prevents oxidation of the sample as was observed in this experiment. Note, however, that on samples where the oxide layer is thinner than about 3 nm, no FIO is observed at the voltage required for a detectable tunneling current. This is in agreement with these models that predict a threshold voltage for the onset of FIO. Note that at these fields, the current is in the direct tunneling regime rather than in the FN regime.

Note that operation in a dry environment currently restricts the operation to a positive gate bias in order to obtain high quality I-V curves and images, making it difficult to investigate the polarity dependence of the tunneling. It is possible, however, that using a metal with a work function lower than Ni, that may also be fashioned into a sturdy CT-AFM cantilever, will reduce the tip-oxide barrier to match that of the silicon-oxide barrier, thus hopefully solve the problem of current spiking. It was also noted in the course of this work that placing a baked sample in a wet environment allowed the observation of negative gate bias curves that would be expected from a dry environment for a few minutes before the oxide absorbed the ambient moisture.

IV. SUMMARY

It was demonstrated that operating a CT-AFM-based, Fowler–Nordheim characterization system in a humid environment modifies the sample under study by field-induced oxidation and is susceptible to variations in surface water coverage. It has also been shown that these processes can be minimized by operating on baked samples in a dry environment.

ACKNOWLEDGMENTS

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