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J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek et al.

Citation: *Appl. Phys. Lett.* **56**, 2001 (1990); doi: 10.1063/1.102999

View online: <http://dx.doi.org/10.1063/1.102999>

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Modification of hydrogen-passivated silicon by a scanning tunneling microscope operating in air

J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, and J. Bennett
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

(Received 27 December 1989; accepted for publication 4 March 1990)

The chemical modification of hydrogen-passivated n -Si (111) surfaces by a scanning tunneling microscope (STM) operating in air is reported. The modified surface regions have been characterized by STM spectroscopy, scanning electron microscopy (SEM), time-of-flight secondary-ion mass spectrometry (TOF SIMS), and chemical etch/Nomarski microscopy. Comparison of STM images with SEM, TOF SIMS, and optical information indicates that the STM contrast mechanism of these features arises entirely from electronic structure effects rather than from topographical differences between the modified and unmodified substrate. No surface modification was observed in a nitrogen ambient. Direct writing of features with 100 nm resolution was demonstrated. The permanence of these features was verified by SEM imaging after three months storage in air. The results suggest that field-enhanced oxidation/diffusion occurs at the tip-substrate interface in the presence of oxygen.

In this letter we report on a novel scheme for nanometer-scale patterning of H-passivated silicon surfaces using a scanning tunneling microscope (STM) operating in air and in an oxygen ambient. Previously reported schemes for STM pattern generation on silicon include organometallic deposition,^{1,2} exposure of resist,^{3,4} and mechanical material removal⁵ of silicon. A significant feature of the present work is the demonstration that a localized chemical change can be confined to a depth of a few nanometers below the surface. Processing strategies exploiting this localized pattern generation may be possible within the context of a unique, STM-based nanotechnology.

The n -Si (111) samples, $\rho = 0.006$ – $10 \Omega \text{ cm}$, were passivated in dilute hydrofluoric acid after an RCA clean.^{6,7} Time-of-flight secondary-ion mass spectrometry (TOF SIMS) analysis of the chemical composition of the passivated surfaces is consistent with recent results using x-ray photoelectron spectroscopy (XPS),^{8–10} high-resolution electron energy loss spectroscopy,⁸ and internal reflection spectroscopy.^{11,12} These results indicate that hydrogen termination dominates the surface bonding structure and provide evidence for direct Si—OH and Si—C bonding. No fluorine was detected.

The STM used in these experiments is a commercially available instrument.^{13(a)} Mechanically fractured^{13(a)} and chemically etched^{13(b)} PtIr tips were used. STM imaging was performed in constant height mode typically with $V_{\text{bias}} = 1.7 \text{ V}$ (tip positive) setpoint current $I = 3 \text{ nA}$, and a scan rate of 3 Hz. Modification of the passivated semiconductor surface occurs during STM imaging in air, as shown in Fig. 1. STM images of test patterns consisting of 200-nm-wide parallel lines spaced 300 nm apart and a $100 \times 100 \text{ nm}$ square feature are shown in Figs. 1 (a) and 1 (b). These features were written with a V_{bias} of 3.5 V and imaged at 1.7 V. A larger pattern, consisting of a $650 \times 650 \text{ nm}$ square superimposed on a $3.5 \times 3.5 \mu\text{m}$ square, was written and then imaged with the STM [Fig. 1 (c)] and with a SEM [Fig. 1 (d)]. The minimum definable feature is currently limited to a $100 \times 100 \text{ nm}$ square by the 10–50 nm residual texture remaining after passivation. It should be possible to produce

smoother surfaces by including a post-oxidation annealing step¹⁴ prior to the passivation step. The patterned areas are quite stable: features could be easily relocated in a SEM after more than three months storage in air.

Since STM images may contain a convolution of electronic and topographic information, an alternate technique, based on a different contrast mechanism, is required to interpret the images. STM-patterned features appear in STM images as 1–20 nm deep depressions in the unmodified substrate. Complementary information from SEM imaging has shown that the features are essentially sources of enhanced secondary-electron yield rather than topographical features.

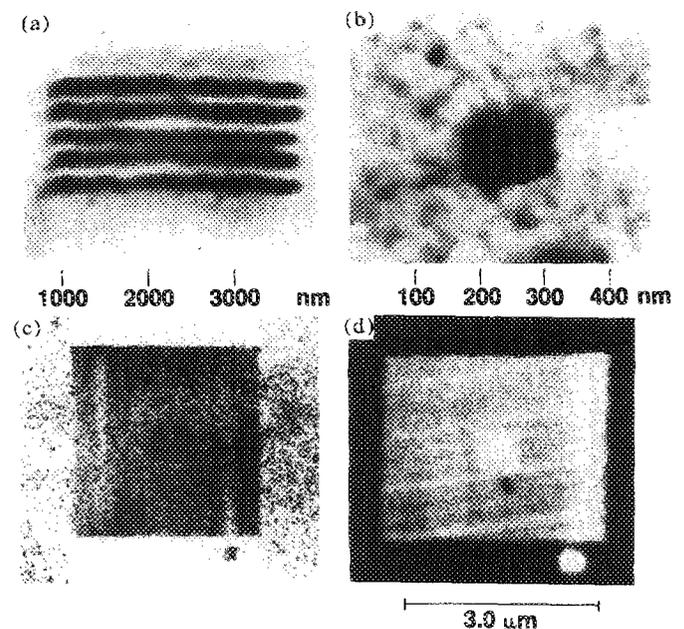


FIG. 1. Features patterned on H-passivated, n -Si (111), $\rho = 10 \Omega \text{ cm}$, using a STM in air. Features were written using $V_{\text{bias}} = 3.5 \text{ V}$ and imaged at 1.7 V, $I = 3 \text{ nA}$ with a 3 Hz scan rate. (a) STM image of a series of 200-nm-wide lines spaced approximately 300 nm apart. (b) STM image of a $100 \times 100 \text{ nm}$ square feature. (c) STM image and (d) field emission SEM micrograph (1.5 keV, line scale, $3.0 \mu\text{m}$) of a $650 \times 650 \text{ nm}$ square superimposed on a $3.5 \times 3.5 \mu\text{m}$ square.

In addition, STM work function measurements [i.e., $d(\ln I)/dS|_v$, where S is the tip-sample distance] taken at modified and unmodified points on the surface indicate a lower work function in the modified regions. Because the reduced work function coincides with an apparent surface depression, we can conclude that a local electronic or chemical change has occurred.

Current-voltage characteristics at the tip-sample interface were obtained for n - and p -doped silicon surfaces and are in agreement with those reported by Kaiser *et al.*¹⁴ Since the tip-sample interaction exhibits the rectifying behavior of a metal-insulator-semiconductor (MIS) structure,^{14,15} a substantial minimum forward bias is required to raise the bottom of the conduction band close enough to the top of the Schottky barrier so that sufficient conduction, in the form of thermionic¹⁶ or tunneling¹⁵ current, can occur. For 3 nA tunnel current in our n -Si (111) samples, we find that $V_{\text{bias}} > 500$ mV is required for imaging. At low bias voltages (< 1.7 V), the tip is very close to, or may actually contact, the surface. Near-contact at low imaging voltages distorts the apparent depth of an imaged feature, as indicated by the lower curve in Fig. 2.

Writing on passivated surfaces proceeds in air or oxygen ambients as a function of bias voltage, as indicated by the upper solid curve in Fig. 2. For $1.7 \text{ V} < V_{\text{bias}} < 3.5 \text{ V}$, the apparent depth of STM-patterned features is a linear function of the bias voltage. Below 1.7 V, the apparent feature depth increases with decreasing voltage, as it does in the imaging curve. This is a result of the current-voltage dependence of the tip-sample distance S for semiconductors.¹⁵

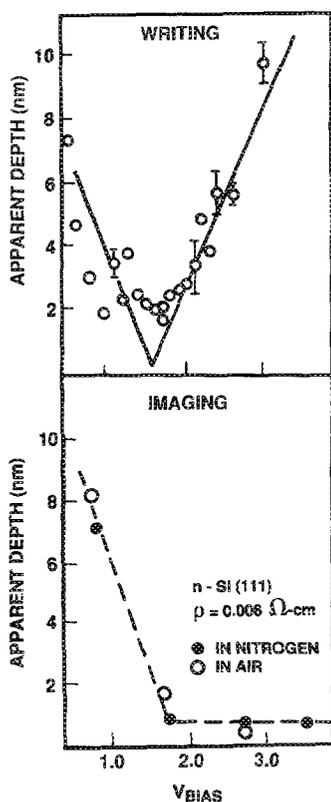


FIG. 2. Apparent depth dependence of STM-produced features as a function of writing voltage (upper curve) and imaging voltage (lower curve) on H-passivated n -Si (111), $\rho = 0.006 \Omega \text{ cm}$ surfaces.

The STM surface modification involves the incorporation of ambient oxygen into the substrate. Figure 3 demonstrates the oxygen partial pressure dependence of the STM-measured depth of the features, and also suggests that the process is enhanced by the presence of water vapor in the air.¹⁷ The data are consistent with an adsorption-limited process.

A TOF SIMS ion map for O^- (m/z 16) is shown in Fig. 4. Several $9 \times 9 \mu\text{m}$ features patterned on silicon are visible in the image, indicating that these features are regions of enhanced oxygen yield relative to the unmodified substrate. The SIMS map was acquired in the static mode, consuming approximately a monolayer of material. After obtaining the map, features could not be relocated, indicating that they are confined to a shallow region just below the surface.

The exact type of bonding involved in oxygen incorporation into the surface is under current investigation. However, two preliminary observations suggest diffusion-enhanced oxidation as a likely mechanism. First, the STM modification of passivated silicon requires the dissociation and/or ionization of oxygen below the tip. A highly localized electric field exists within the tip-sample gap during tunneling which may cause the diffusion of oxygen ions into the high-field region. The surface OH groups are nucleating sites^{8,17} on the otherwise hydrophobic, passivated surface. Thus, the local reaction rate may be enhanced at OH sites below the tip. Second, the properties of STM-modified regions are virtually indistinguishable from SEM beam-induced changes on the same passivated surfaces with respect to lack of topography, enhanced secondary electron yield, and resistance to chemical etching. Beam-enhanced oxygen diffusion into clean silicon substrates is well known from Auger studies.¹⁸⁻²⁰ In fact, we have found that freshly passivated silicon surfaces are extremely susceptible to SEM beam-induced changes, presumably due to the presence of OH groups⁸ on the surface. Thus, it is likely that the STM features are the result of a locally enhanced surface oxidation.

Pattern definition is meaningful only if the modified re-

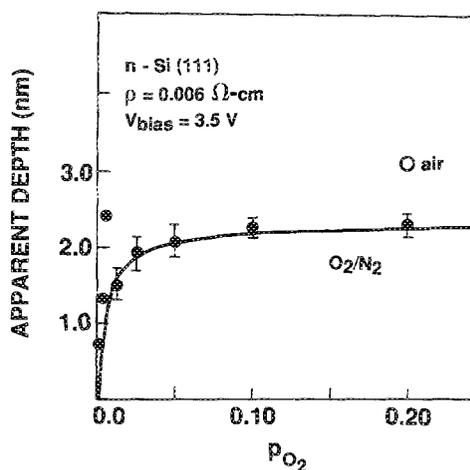


FIG. 3. Apparent depth of features produced on a H-passivated, n -Si (111), $\rho = 0.006 \Omega \text{ cm}$ surfaces with a STM as a function of oxygen partial pressure (filled circles) and in air (open circle). The solid curve has the form of a Langmuir adsorption isotherm and is given by $2.3/(1 + 0.8/p_{\text{O}_2})$. Features were written at a $V_{\text{bias}} = 3.5$ and imaged at 1.7 V.

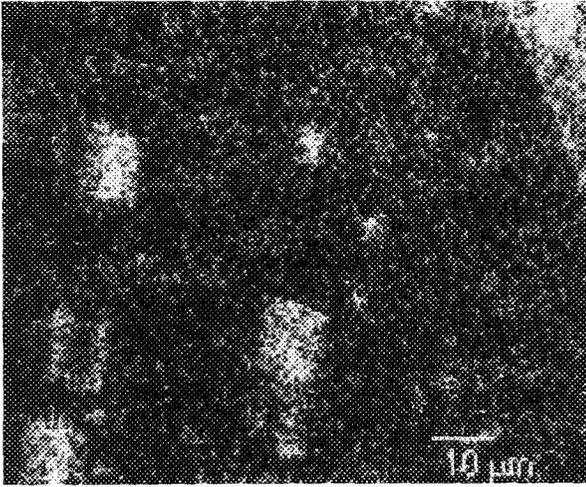


FIG. 4. TOF SIMS ion map for oxygen, O^- (m/z 16), of a region of a H-passivated, n -Si (111), $\rho = 10^{-3} \Omega \text{ cm}$, surface containing four $9 \times 9 \mu\text{m}$ features written with a STM at $V_{\text{bias}} = 3.5 \text{ V}$, $I = 3 \text{ nA}$ in air. TOF SIMS ion map dose was approximately 10^{14} ions/cm².

regions are chemically distinct from the unmodified substrate. The STM-patterned features can be etched selectively by a 15 s dip in $\text{HNO}_3:\text{HOAc}:\text{HF}$ (5:3:3) to produce submicron-deep topographic features which could be located by Nomarski microscopy. We consider the demonstration of STM pattern development on silicon to be a significant result of this work.

In conclusion, we have produced stable, low-voltage, nanometer-scale chemically modified features on passivated semiconductor surfaces using a STM in air. The features have been characterized by STM spectroscopy, SEM, and TOF SIMS. We have shown that oxygen incorporation into the silicon surface produces a chemical modification which may be selectively etched, suggesting that development of a unique, STM-based nanotechnology is possible.

The authors wish to thank L. Richter (NIST) for providing samples during the early stages of this work, and R. D. Larrabee, D. E. Newbury, and B. Penzes (NIST), E.

Ehrichs and A. L. de Lozanne (U. Texas), R. J. Colton and C. R. K. Marrian (NRL) for helpful discussions.

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- ¹³(a) Digital Instruments Inc., Santa Barbara CA 20878. (b) Custom Probes Unlimited, Gaithersburg MD 20899. Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
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