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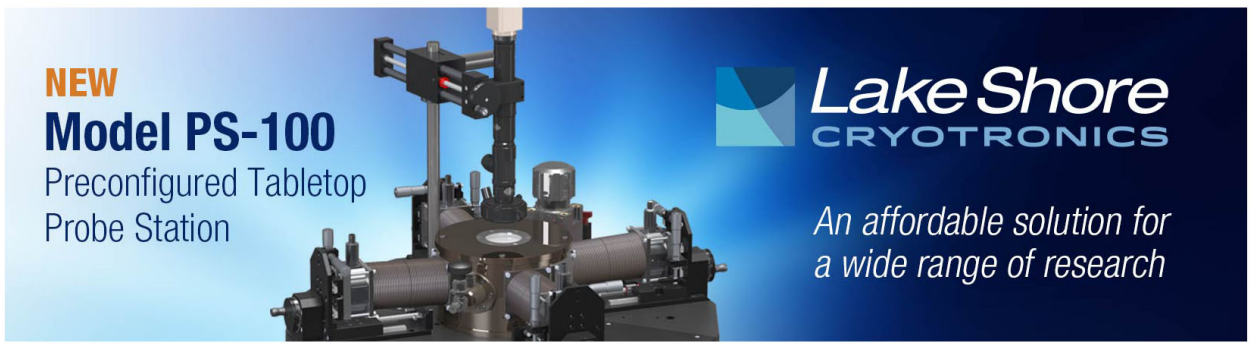

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Nanoscale patterning and oxidation of H-passivated Si(100)-2×1 surfaces with an ultrahigh vacuum scanning tunneling microscope

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Nanoscale patterning of the hydrogen terminated Si(100)-2×1 surface has been achieved with an ultrahigh vacuum scanning tunneling microscope. Patterning occurs when electrons field emitted from the probe locally desorb hydrogen, converting the surface into clean silicon. Linewidths of 1 nm on a 3 nm pitch are achieved by this technique. Local chemistry is also demonstrated by the selective oxidation of the patterned areas. During oxidation, the linewidth is preserved and the surrounding H-passivated regions remain unaffected, indicating the potential use of this technique in multistep lithography processes.

The scanning tunneling microscope (STM) has evolved from an atomic resolution imaging tool into one that is capable of modifying surfaces on the atomic to nanometer size scale. This represents a potential step forward in the effort to push nanofabrication schemes into the sub-0.1 μm regime. To date, a variety of STM-based lithography schemes have been tested, utilizing current, electric field, electron energy, or mechanical force to modify surfaces.[1] For silicon, the best resolution is achieved under ultrahigh vacuum (UHV) conditions, where clean surfaces can be prepared and spurious chemical reactions avoided. This has been demonstrated by Avouris and Lyo who have developed a technique to extract individual or small clusters of adatoms from the Si(111)-7×7 surface by applying voltage pulses to the tip while in tunneling range.[2] These atoms reside on the tip until an opposite polarity pulse deposits them elsewhere on the surface. A similar technique, developed recently by Aono *et al.*, also uses atom extraction to pattern grooves in the Si(111)-7×7 surface.[3] Although these experiments demonstrate nanometer scale resolution, they are perturbative to both the tip and surface structures. This letter reports a less perturbative approach to achieving nanoscale patterning of silicon, by using the STM to selectively desorb hydrogen from a UHV-passivated Si(100)-2×1:H surface. The hydrogen remaining on the surface acts as a mask, opening numerous possibilities for selective chemistry to be performed on the nanometer size scale.

A precedent for the results reported here is the work of Dagata *et al.*[4] in which ambient STM lithography was performed on wet chemically passivated silicon surfaces. This resulted in the formation of a 1–2-monolayer (ML)-thick oxide, with linewidths of about 100 nm.[4] Recently, Snow *et al.* have extended this technique by combining it with wet chemical etching to create 15-nm-deep grooves on a 50 nm pitch.[5] Similar experiments by Day and Allee[6] and by Fay *et al.*[7] utilized a thicker patterned oxide, and achieved pattern transfer either by HF etching,[6] thermal oxidation,[7] or reactive ion etching,[7] using the oxide as a mask. In these latter experiments, the tip triggers the anodic oxidation of the silicon surface by the adsorbed ambient species.[6,7] The minimum linewidths achieved in these experiments are in the 20–25 nm range.[5,7]

Becker *et al.*[8] and Boland[9] have extended the STM depassivation of silicon into UHV. Becker's group has shown that under careful handling conditions atomic resolution STM images can be obtained in UHV for wet chemically passivated Si(111)-1×1:H surfaces.[8] Furthermore, they mentioned the ability to depassivate areas as small as 40 Å in diameter with the STM tip, resulting in the local conversion of the surface into the Si(111)-2×1 structure. Boland has shown that hydrogen can be desorbed by the STM tip from a Si(111)-7×7:H surface that has been H-passivated under UHV conditions.[9]

This letter reports the results of UHV STM nanolithography experiments on hydrogen passivated Si(100)-2×1:H surfaces. This surface is readily prepared in UHV, and has better structural and electronic uniformity than the Si(111)-7×7:H surface. UHV surface preparation and hydrogen passivation avoids the contamination issues associated with wet chemical processing. Our experiments were performed on boron-doped Si(100) samples (0.1 Ω cm).[10] The clean Si(100)-2×1 surface was prepared by heating the sample to 1250 °C for one minute, while maintaining a background pressure below 3×10^{-10} Torr. The STM experiments were performed at a base pressure of 5×10^{-11} Torr. Atomic hydrogen for dosing was created by cracking molecular hydrogen with a 1500 °C W filament placed 6 cm away from the sample surface. During this procedure, the UHV chamber was back filled with 1×10^{-6} T of H_2 and the total H_2 dose ranged from 400–1200 L [1 Langmuir (L)$=1\times10^{-6}$ Torr s]. Although the exact atomic hydrogen dose was not measured, doses above 400 L ensured saturation coverage of the surface. To prevent the formation of higher hydrides and surface etching, the silicon sample was heated to 650 K while dosing. At this temperature, only the surface π bond of each silicon dimer atom reacts with hydrogen, forming the uniform monohydride surface. This is well known from earlier surface studies,[11] and has also been observed in the STM work of Boland.[12]

The STM used for these experiments is a UHV adaptation of the design developed in our laboratory[13] and

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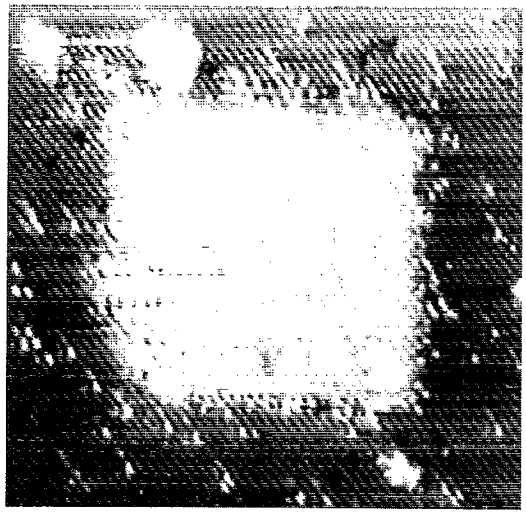

FIG. 1. A 400 Å×400 Å STM image of a Si(100)-2×1:H surface showing a 230 Å×230 Å STM depassivated area. The depassivation was performed as a series of 21 evenly spaced lines, using a tip bias of −5.5 V, 1.0 nA, and a line dose of 1×10^{-3} C/cm. The image was acquired at −2 V sample bias and 0.1 nA.

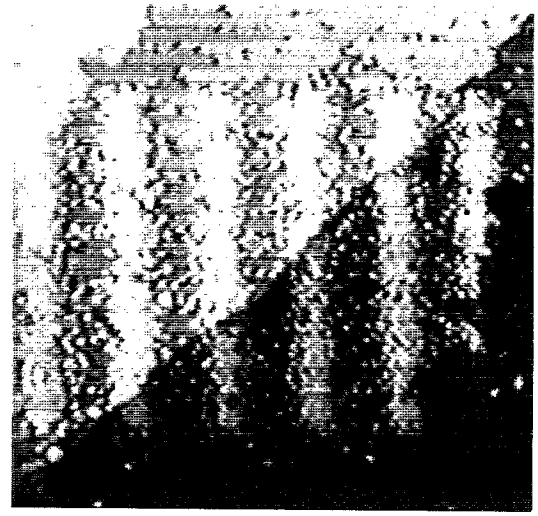

FIG. 2. A 600 Å×600 Å STM image showing set of STM depassivated lines spaced on a 100 Å pitch. The lines were depassivated at −7 V tip bias, 0.1 nA, and a line dose of 1.0×10^{-4} C/cm.

equipped with two-dimensional (2D) coarse translation of the probe over mm distances.[14] Dc-etched W tunneling probes were used, having typical radii of curvature ranging from 30–150 Å, as verified by transmission electron microscope measurements.[15] All of the STM images presented in this letter were obtained under constant current scanning conditions, at a current of 0.1 nA. During STM pattern generation, the feedback servo loop is not interrupted, and all transitions between patterning and normal scanning conditions are accomplished in a smooth manner, within the servo loop bandwidth. This procedure gives highly reproducible results while preventing degradation of the tunneling probe.

Figure 1 shows a 400 Å×400 Å image of a Si(100)-2×1:H surface in which a 230 Å×230 Å square has been depassivated at a tip bias of −5.5 V with respect to the sample. A current of 1.0 nA was used to write this pattern as a series of 21 evenly spaced lines. A line dose of 1×10^{-3} C/cm was used, corresponding to an area dose of 8×10^{3} C/cm^2. This dose is quite high when compared to traditional electron beam lithography, however the high current density of the STM makes such doses easily accessible. In our experiments, writing speeds of 0.01–1 μm/s are typically used. Figure 1 clearly shows that the Si dimer rows are continuous throughout the patterned and unpatterned areas. The patterned square appears brighter (1.5 Å higher) since depassivation restores the clean surface π-bonded state, increasing the efficiency of electron transfer between the probe and surface. We have also performed $(dI/dV)/(I/V)$ spectroscopy in the depassivated areas, observing the restoration of the clean surface π_b dangling bond peak at −0.8 eV. From our experience with many areal patterns like that of Fig. 1, we observe no evidence for repassivation of the surface by liberated hydrogen. This supports an associative recombination mechanism in which H_2 is evolved, as shown previously in thermal desorption studies of hydrogen from the Si(100)-2×1:H monohydride surface.[16,17] The sharp definition of the pattern boundaries in Fig. 1 suggests the possibility of performing higher resolution lithography. This is demonstrated in Fig. 2 where a pattern of 40–50-Å-wide parallel lines, spaced on a 100 Å pitch, was written at a tip bias of −7 V and 0.1 nA. A line dose of 1×10^{-4} C/cm was used in this case, an order of magnitude less than that used for the Fig. 1 pattern. The conversion efficiency for depassivation in this case is 2.3×10^{6} electrons per removed hydrogen atom, an order of magnitude less than that measured for the Si(111) case.[8] From a series of patterning experiments in which only the tip bias was varied, we have inferred that depassivation occurs when the classical electron energy exceeds the Si—H bond strength, $E_{\mathrm{Si—H}} = 3.5–3.8$ eV.[17] The 3–4 eV barrier heights that we measure for our tips, indicate a depassivation threshold ranging between −6.5 and −7.5 V tip bias, assuming an ideal trapezoidal barrier shape. We typically observe a lower depassivation threshold, between −5.5 and −6.5 V, consistent with a realistic, nontrapezoidal barrier. It is interesting to note that the depassivation threshold is closer to the Si—H bond strength than the bonding-antibonding energy separation of about 5.5 eV,[18] unlike the case of the Si(111)-1×1:H surface.[8] A detailed understanding of the depassivation mechanism will require further experiments and associated theoretical treatments.

Depassivation can also be achieved at lower voltages if higher currents are used. In this case, the feedback servo loop moves the tip closer to the sample, resulting in partial collapse of the barrier. We generally observe the highest patterning resolution under these conditions. This is illustrated in Fig. 3 for patterns written at −4.5 V, 2 nA, and a dose of 2×10^{-3} C/cm. Figure 3(a) shows a grid of ~10-Å-wide lines patterned on a 30 Å pitch, and Fig. 3(b) shows the letters 'UI ONR URI' patterned with the same linewidth. The improved resolution is most likely the result of reduced beam divergence associated with closer tip to sample spacing. We are currently investigating the details of dose, electron energy,

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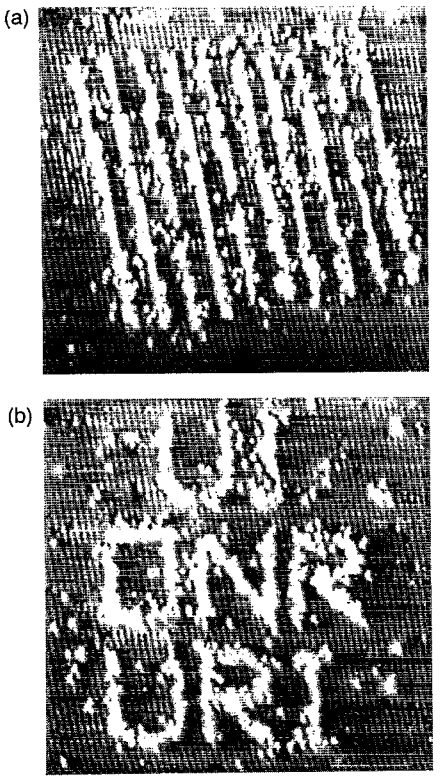

FIG. 3. High resolution patterns written at −4.5 V tip bias, 2.0 nA, and a line dose of 2×10^{-3} C/cm. (a) 10 Å-wide lines spaced on a 30 Å pitch, and (b), the letters 'UI ONR URI' written with the same linewidth. The images are 400 Å×400 Å.

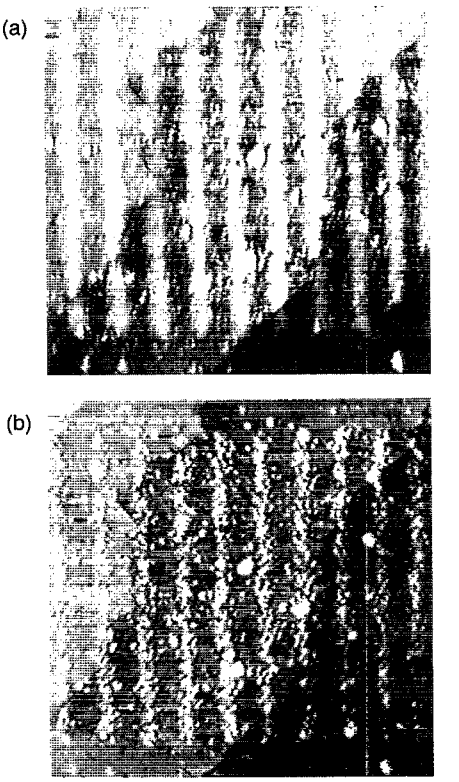

FIG. 4. STM patterned lines (a) before, and (b) after a 100 L O_2 dose. The image size is 800 Å ×800 Å, and the lines are spaced on a 80 Å pitch.

barrier effects, and resolution for this system.[19] In all cases, we only observe depassivation when the tip is biased negative with respect to the sample, supporting the hypothesis that electron energy plays the key role. Positive tip biases up to 10 V have no effect on the surface in our experiments.

The restoration of the clean Si(100)-2×1 surface, by STM depassivation of hydrogen, suggests numerous chemical modification schemes. We have examined one possibility in which the STM-patterned surface is exposed to molecular oxygen. Figure 4 shows a comparison of a pattern of 80 Å pitch parallel lines before and after exposure to 100 L of O_2. It is clearly evident that the patterned lines are affected by oxygen exposure, appearing irregular along their length when compared to the freshly depassivated lines. These changes are most likely electronic effects associated with the initial oxidation reaction, and are under further study in our laboratory. It is important to note that the hydrogen passivation is impervious to O_2 dosing and that the patterned linewidth remains unchanged after oxygen exposure.

In summary, this letter demonstrates 1 nm linewidths and selective oxidation for STM depassivated Si(100)-2×1:H surfaces. The STM patterning depends on electron energy, indicating the potential use of this technique with other low-energy electron beam systems. We have benefited from discussions with Professor Karl Hess, Dr. Phil Scott, and Dr. Steve Skala. This work is supported by the Office of Naval Research University Research Initiative under Grant N00014-92-J-1519.

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