Extending Feedback-Controlled Lithography to Ambient Conditions

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Abstract

Feedback-controlled lithography (FCL) enables atomically precise patterning of individual molecules on the technologically significant Si(100)-2 x 1:H surface. However, because it is performed in an ultrahigh vacuum (UHV) environment, FCL has thus far been restricted to surface chemistries that can be delivered in the gas phase. The present research attempts to introduce a new class of chemical and biological molecules — those suspended in liquid solvent — for use in FCL nanopatterning. Specifically, the Si(100)-2 x 1:H surface is removed from its native UHV environment and is subjected to liquid-phase chemical processing under atmospheric pressure conditions. A custom experimental setup, consisting of a UHV scanning tunneling microscope (STM) chamber that is directly interfaced to an inert atmosphere glovebox, facilitates liquid-phase chemical processing without exposing the pristine hydrogen monolayer to air-induced oxidation. While in the inert atmosphere, the Si(100)-2 x 1:H surface is treated with a variety of organic and aqueous solvents. Atomic resolution STM images reveal that the hydrogen passivation remains largely intact after treatments in toluene and dichloromethane. In addition, by minimizing oxygen levels during processing, perturbation to the Si(100)-2 x 1:H surface can be significantly reduced following exposure to water. This study delineates the conditions under which various organic and biological molecules can be delivered to nanopatterned Si(100)-2 x 1:H surfaces via liquid-phase solvents.

Introduction

The scanning tunneling microscope (STM) recently enabled the world's highest-resolution room-temperature nanolithography — feedback-controlled lithography (FCL).[1,2] On hydrogen-passivated Si(100), FCL locally desorbs individual hydrogen atoms via electron-stimulated desorption to generate arbitrary arrays of dangling bonds like the 3 x 3 array in Figure 1. Because this is performed in ultrahigh vacuum (UHV) conditions, these sites will remain unterminated until molecules are intentionally introduced into the chamber. The highly reactive dangling bonds, compared with the relatively inert hydrogen passivation, covalently bind and immobilize the gas-phase molecules. Such precise, selective control over surface chemistry may lead to sensors that can detect the presence of a single molecule — the ultimate sensitivity for security and medical applications.

Unfortunately, many chemical and biological molecules thermally decompose or have vapor pressures too low for UHV deposition, which subsequently precludes the patterning of some of the most technically relevant molecules (e.g., polymers, volatile organics, and biological materials). These molecules are better suited for deposition from a wet-chemical solution in ambient atmosphere (i.e., standard temperature and pressure) as opposed to in vacuum. Only recently has it been shown that, with proper precautions against bombardment by energetic-free radicals, the Si(100)-2 x 1:H surface may be moved from UHV into ambient atmosphere without compromising its atomic-level purity.[3]

This research is an extension of work from the summer 2002 NSEC internship and reports the first successful STM images of the UHV-prepared Si(100)-2 x 1:H surface following wet-chemical solvent exposures in ambient atmosphere. As a demonstration of feasibility for future combinatorial UHV and wet-chemical processing, this research establishes that the surface is sufficiently stable to be moved from UHV into ambient conditions and treated with a number of widely used solvents without damaging its atomic-scale structure. These initial results suggest that chemical or biological molecules may be deposited onto the surface from suspension in toluene, dichloromethane, or water.

Background

The theoretical phase of this project was conducted during the MIN program of summer 2002.

Robustness of the Si(100)-2 x 1:H Surface to Ambient Atmospheres

In order to pattern "soft" material from wet-chemical solution, the surface must be removed from the UHV chamber and transferred into an ambient environment. Bringing the surface into ambient air is the most convenient approach. In this study, a freshly passivated Si(100)-2 x 1:H surface (seen in Figure 2a) was transferred from the nitrogen-vented load-lock and held in atmospheric air for 15 minutes, followed by a 12-hour in situ degas at about 200°C to remove any weakly physisorbed atmospheric species prior to STM imaging. Figure 2b shows that the surface appears damaged, with an increased density of both point and broken dimer

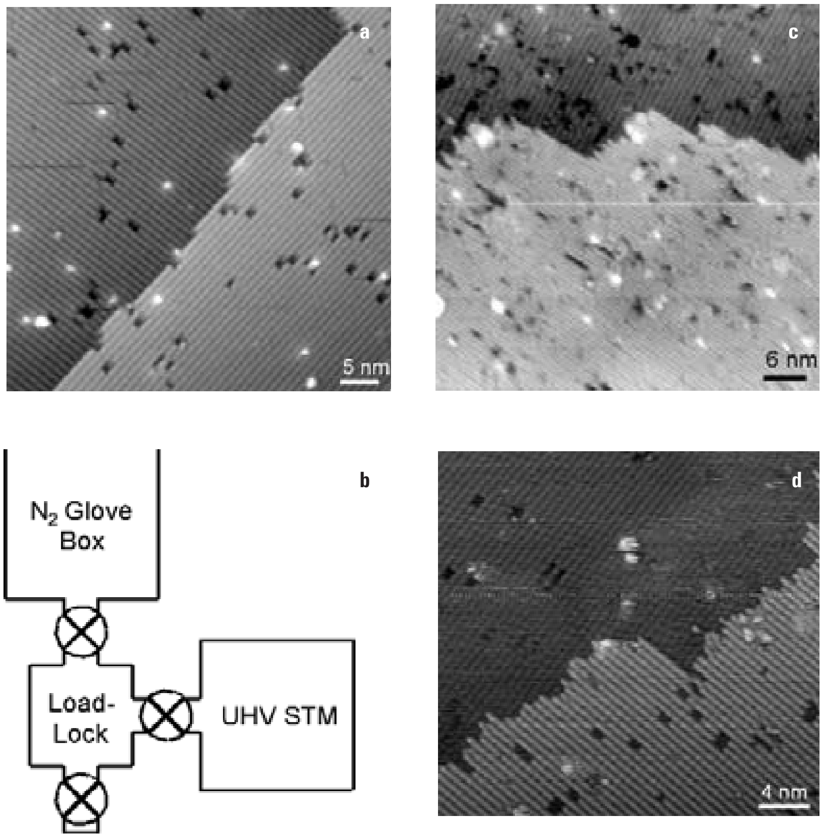

Figure 2: UHV STM images [–2V, 0.1nA] of the Si(100)-2 x 1:H surface, (a) before and, (b) after exposure to atmospheric air for 15 minutes followed by a 12-hour degas at ~200˚C in UHV. The surface passivation appears severely degraded. (c) An ambient nitrogen glovebox (760 Torr, 0.4 ppm oxygen, 0.5 ppm water vapor) is directly interfaced to the load-lock, allowing transfer between the ambient and UHV environments without exposure to air. (d) UHV STM image [–2 V, 0.1 nA] of a newly passivated surface after it was transferred into and held in the glovebox for 45 minutes shows that the ambient nitrogen exposure does not appreciably affect the surface. The relative defect density resembles that of an as-prepared surface.

defects after the air exposure. It is known that the presence of oxygen and water vapor in air accelerates oxide growth on hydrogen-passivated silicon[4, 5] and may be responsible for the visible damage.

In light of these results, the load-lock of the UHV chamber was interfaced to a glovebox with a dry nitrogen ambient (~760 Torr) atmosphere, depicted in Figure 2c. From the nitrogen-vented load-lock, a freshly passivated sample was transferred directly to the glovebox and was never exposed to oxygen and water vapor concentrations greater than 0.4 ppm and 0.5 ppm, respectively. Figure 2d shows the surface after a 45-minute exposure to atmospheric dry nitrogen in the glovebox. The sample's relative defect density is comparable to that of the typical as-prepared surface of Figure 2a, and its overall quality greatly exceeds that of the air-exposed surface despite a three-times-longer exposure time.

Robustness of the Si(100)-2 x 1:H Surface to Solvent Treatments

After establishing the glovebox as a sufficiently inert workplace for future ambient processing, the next requirement for wet-chemical patterning is ensuring that the solvents do not attack the Si(100) surface's hydrogen passivation. In this study, the organic solvents toluene and dichloromethane were distilled in a dry nitrogen environment over sodium/benzophenone and calcium hydride, respectively. The solvents were stored in airtight bulbs under nitrogen and transferred into the glovebox. All lab ware, which was either glass or solid Teflon, had been cleaned by 15-minute ultrasonications in acetone and isopropanol, followed by rinsing in ultrapure water. A freshly passivated Si(100)-2 x 1:H surface was moved directly into the glovebox. There, 200 liters of neat solvent were pipetted directly onto the sample surface to ensure complete coverage for five seconds and then blown dry with a nitrogen stream. The samples were transferred directly back into the load-lock and reintroduced to the UHV STM within 30 minutes of initial venting. Prior to imaging, the samples were degassed at about 200°C for 12 hours. This entire procedure was performed for both neat solvents.

Figures 3a and 3b show two Si(100)-2 x 1:H surfaces after direct exposure to toluene and dichloromethane, respectively. In both images, the hydrogen passivation is not directly visible, and both surfaces appear generally flat. On the toluene-exposed surface, a measurement of the vertical height between adjacent terraces suggests that the distance is preserved. For an ideal Si(100)-2 x 1:H surface, the step height is 1.4 Å, and in Figure 3a, the average is 1.5 ± 0.3 Å. Additionally, on the dichloromethane-exposed surface, two atomic step edges are clearly visible. Both of these images suggest that the solvents did not directly attack the surface; rather, a layer of physisorption is merely obscuring the underlying passivation. This most likely arises from residual organic contamination that the solvents picked up from beakers and pipettes in ambient atmosphere.

Experimental Phase

The experimental phase of this NSEC MIN project was conducted during school year 2002-03.

In an attempt to minimize the ambient contamination problem of the previous experiments, a more stringent cleaning regimen was employed. Ultrapure water was used to rinse all lab ware after each 15-minute ultrasonication in acetone, isopropanol, methanol, and ethanol. The lab ware was then boiled in a 1% sodium peroxodisulfate ($Na_2S_2O_8$) aqueous solution, rinsed in ultrapure water, and blown dry with nitrogen. Afterward, the containers were stored in an 80°C oven until immediately prior to use. It is known that boiling $Na_2S_2O_8$ aqueous solution decomposes organic contamination on the surfaces of lab ware involved in the wet-chemical passivation of defect-free Si(111):H surfaces.[6] The toluene and dichloromethane exposures were repeated for five seconds each.

Figures 4a and 4b reveal that the Si(100)-2 x 1:H surface is virtually unaffected by the five-second exposures to toluene and dichloromethane, respectively. In both cases, the alternating monohydride dimer row structure and defined-step edges are still clearly evident. The relative defect densities after solvent exposures are similar to those for a freshly passivated surface. Notably, the previously unterminated silicon bonds, which were likely capped by trace water or oxygen molecules during load-lock venting, did not serve as nucleation sites for larger contamination growth.

Although chemisorption of organic solvents to the hydrogenated silicon surface may in some instances be thermodynamically favorable (e.g., Si-C is 1.59 eV less than Si-H),[7] the fact that hydrogen-passivated dimers remain intact after solvent treatment indicates that the activation barrier for covalent reaction is well above the available thermal energy at room temperature in the liquid system.

On the same area of the dichloromethane-treated surface of Figure 4b, electron stimulated desorption (ESD) with the tip of the STM is used to intentionally break

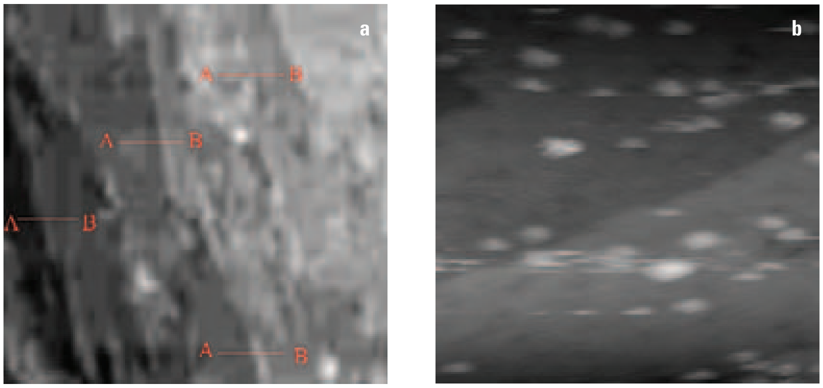

Figure 3: Two UHV STM images [(400Å)^2, -2V, 0.1nA] of Si(100)-2 x 1:H following wet-chemical exposure to (a) toluene and (b) dichloromethane. Although the hydrogen passivation is not directly visible, the vertical step height in (a) is approximately equal to that of an ideal surface, and two atomic step edges are apparent in (b).

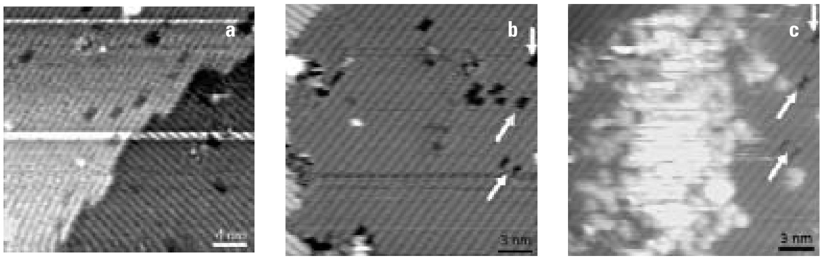

Figure 4: STM images of the Si(100)-2 x 1:H surface that was transferred directly from UHV into an inert-atmosphere glovebox, where it was treated for five seconds with (a) toluene [–2.0 V, 0.066 nA], and (b) dichloromethane [–2.2 V, 0.05 nA], followed by a 12-hour degas at ~200ºC in UHV. The surface's hydrogen passivation, including dimer rows and an atomic step edge, is unperturbed by the treatments. (c) For comparison, arrows point to the same preexisting defects before and after STM-induced electron stimulated desorption of hydrogen was performed at 6.5 V and 2 nA. This demonstrates the suitability of this surface for nanofabrication even after wet-chemical processing in ambient conditions.

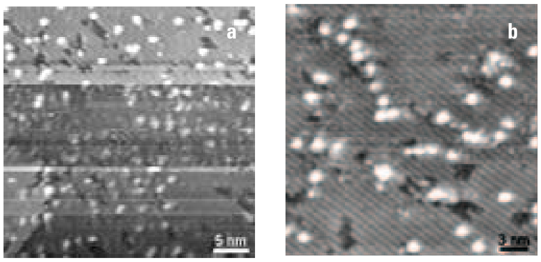

Figure 5: Two UHV STM images [–3.5 V, 0.04 nA] of the Si(100)-2 x 1:H surface after direct transfer from UHV into the glovebox, where it was treated with ultrapure water for five seconds, followed by a 12-hour degas at ~200ºC in UHV. (a) Alternating monohydride dimer rows of adjacent terraces and an atomic step edge (lower left corner) are still clearly evident after the exposure, despite an obvious increase in the number of point defects. (b) Additional broken dimer defects appear sporadically and usually span adjacent dimer rows, rather than proceeding along every other dimer row.

the Si-H bonds and create the line in Figure 4c at bias conditions (6.5 V, 2 nA), which corresponds to the direct electronic excitation regime for H desorption from Si (~6.5 eV).[8] This provides further evidence for the survival of the hydrogen monolayer. Additionally, the quality of these surfaces demonstrably satisfies the pristine conditions necessary for UHV-STM-based lithography, which will allow patterning and nanofabrication even after chemical treatments in ambient conditions.

Water is a very important biological solvent that was also studied as a possible solvent from which to deposit biological molecules. Water (pH 7.0, resistivity=18.2 M Ω-cm) was obtained from a Millipore system and sparged with dry nitrogen for one hour in an attempt to minimize dissolved oxygen. In the glovebox, it was applied to a newly prepared surface for five seconds. The sample was degassed at about 200°C for 12 hours prior to STM imaging. Figure 5 shows the Si(100)-2 x 1:H surface after exposure to water. Despite an obvious increase in the density of both missing dimer and point defects relative to a typical passivated surface, the surface retains a majority of its hydrogen passivation, atomic flatness, and atomic step edges.

From studies of the Si(111):H surface, it is known that the OH^- ions in water form surface silanol species (Si-OH) that polarize the underlying Si-Si back-bonds through the strongly electron-withdrawing oxygen atom.[9,10] Although Fourier-transformed infrared (FTIR) spectroscopy on Si(111):H showed only 0.13 monolayer of silanol after 2,000 minutes in water,[11] the greater local electronic density of silanol relative to the surrounding passivation may partly explain the increase in the number of bright protrusions in the present STM images.

Comparing the relative stabilities of monohydride and dihydride silicon surfaces, the monohydride phase is considerably more resistant to oxidation[12,13] and etching.[10,14,15] A similar experiment on the dihydride Si(100)-1 x 1:H surface showed that a 10-minute rinse with ultrapure water preferentially etches every other row of surface silicon atoms.[16,17] This was attributed to the strong repulsive force between the closely configured dihydride units (1.51 Å nearest H neighbor distance),[18] whose distance is increased and total energy is reduced after etching. Following this reasoning, the monohydride Si(100)-2 x 1:H surface should be more stable in water because of the larger spacing between adjacent monohydrides (3.52 Å nearest H neighbor distance).[19] Accordingly, the increase in missing dimer defects in Figure 5 is not likely caused by the preferential etching phenomenon associated with the dihydride surface, because the depressions appear randomly, are localized, and span adjacent dimer rows. These results may be improved with water of lower pH and more rigorous purification steps. Nevertheless, the quality of the surface in Figure 5 may very well be acceptable for future STM studies of biomolecules intentionally deposited from aqueous solution.

Conclusions

In summary, the robustness of the *in situ* prepared Si(100)-2 x 1:H surface to wet-chemical solvents in ambient atmosphere has been directly observed by UHV/STM as a necessary precondition for patterning chemical and biological molecules from solution. A directly interfaced, dry-nitrogen glovebox permits ambient processing without atmospheric degradation after 45 minutes. When treated with ultrapure water for five seconds, the Si(100)-2 x 1:H surface shows moderate damage but no evidence of the preferential etching typical of the dihydride Si(100)-1 x 1:H surface. The organic solvents toluene and dichloromethane have no appreciable effect on the surface passivation within the five-second exposure time. These initial results suggest that longer treatment times with solvents suspending chemical or biological molecules can be explored. The intrinsic chemical robustness of the Si(100)-2 x 1:H surface, coupled with scrupulously clean processing conditions, enables STM nanolithography following ambient wet chemistry.

Future work will attempt to bind chemical/biological molecules to the Si(100)-2 x 1:H surface from solution with atomic precision. First, FCL will pattern the surface with functionalized “linker” molecules that are UHV compatible. Then, the surface may be transferred into the ambient glovebox, where it may be dipped into a solution of complementarily functionalized “target” molecules of interest. In this way the attachment of these UHV-incompatible molecules will, for the first time, be templated with atomic precision.

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