Atomic-level study of the robustness of the Si(100)-2×1:H surface following exposure to ambient conditions

M. C. Hersam,[a] N. P. Guisinger, and J. W. Lyding
Department of Electrical and Computer Engineering and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, Illinois 61801

D. S. Thompson and J. S. Moore
Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, Illinois 61801

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The *in situ* hydrogen-passivated Si(100)-2×1 surface is characterized with x-ray photoelectron spectroscopy (XPS) and ultra-high-vacuum scanning tunneling microscopy (STM) following exposure to ambient conditions. The XPS measurements illustrate the chemical inertness of this surface as the onset of oxidation is not observed for the first 40 h of ambient exposure. After 15 min of contact with atmospheric conditions, the STM images reveal that the Si(100)-2×1:H surface remains atomically pristine. This exceptional stability is of relevance to a wide variety of applications that require ultrapure Si(100) substrates (e.g., microelectronics, semiconductor processing, nanofabrication, etc.). © *2001 American Institute of Physics.*
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The relentless development of advanced silicon-based technology has placed increasingly stringent cleanliness requirements on Si(100) substrates. As modern microelectronic devices progress towards ultrathin (<20 Å) gate oxides,[1] even atomic-level defects can degrade performance. Silicon-based molecular-beam epitaxy (MBE) systems, which are used to grow device structures that require nanoscale precision (e.g., resonant tunneling diodes), have comparable substrate concerns.[2] Ultra-high-vacuum scanning tunneling microscopy (UHV-STM)-based nanolithography on Si(100)-2×1:H surfaces also requires atomically pristine conditions.[3] For this reason, surface preparation and subsequent processing of UHV-STM-patterned substrates have been limited to the UHV chamber, thus restricting the capabilities and applications of this nanolithographic technique. Consequently, an atomically flat and robust passivating layer for Si(100) substrates could potentially impact many sectors of the silicon research and development community.

Historically, wet-chemical treatments have been the most widely used methods for generating H-passivated Si surfaces. Initial studies on the Si(111) surface demonstrated that treatment with concentrated HF leads to a well-ordered, albeit microscopically rough, termination that includes monohydride, dihydride, and trihydride species.[4] By utilizing HF solutions buffered with NH_4F, further research showed that monohydride Si(111) surfaces can be produced on which atomically flat domains have been detected.[5,6] The production of an atomically flat Si(100) surface, however, has remained elusive. Wet-chemical treatment of Si(100) with buffered HF solutions leads to a surface with dihydride termination.[7] The relative instability of dihydride compared to monohydride species implies that buffered HF etching of Si(100) can easily lead to the formation of pits with (111) facets.[8–10] Although recent results suggest that these pits can be minimized through brief (~1 min) etching in a NH_4F solution,[11] the chemical stability of this optimized dihydride Si(100) surface has not yet been reported.

This letter studies the robustness of the *in situ* prepared monohydride Si(100)-2×1:H surface following exposure to ambient conditions. Previous infrared spectroscopy measurements on H-passivated Si(100) surfaces generated by high-temperature (1050 °C) annealing in a H_2 atmosphere suggest that the monohydride surface is particularly resistant to oxidation and hydrocarbon contamination.[12,13] This letter extends these results by studying the oxidation resistance of the Si(100)-2×1:H surface with x-ray photoelectron spectroscopy (XPS). Furthermore, the STM measurements illustrate that the monohydride Si(100) surface remains atomically flat and clean even following removal from the UHV environment.

Hydrogen passivation was accomplished in an UHV chamber with a base pressure of 5×10^{-11} Torr on heavily doped Si(100) samples.[14] The clean Si(100)-2×1 surface was prepared by annealing the sample *in situ* at ~1250 °C for 30 s. Molecular hydrogen was then leaked into the UHV chamber and cracked on a hot (~1500 °C) tungsten filament positioned about 6 cm away from the Si surface. During the atomic H dose, the sample temperature and the chamber pressure were stabilized at 650 K and 2×10^{-6} Torr, respectively, for 10 min. STM imaging confirmed that a fully monohydride-passivated surface resulted from these processing conditions.

For the oxidation resistance study, the sample was moved from the UHV chamber into ambient conditions. The sample was periodically checked with XPS to monitor the extent of surface oxidation, as shown in Fig. 1. For comparison purposes, the bottom trace of Fig. 1 illustrates an XPS spectrum of a Si(100) sample that possesses a native oxide.

[a]Current address: Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108; electronic mail: m-hersam@northwestern.edu

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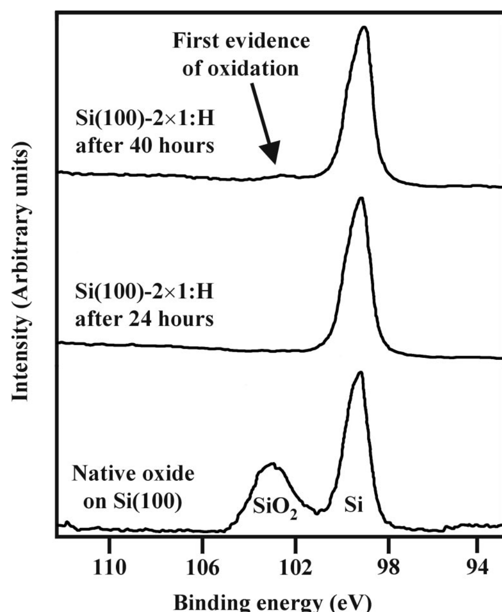

FIG. 1. Upper two XPS spectra show the stability of the Si(100)-2×1:H surface against oxidation. A faint oxide peak only becomes apparent after 40 h of exposure to ambient conditions. For comparison, the bottom XPS spectrum depicts the oxide peak generated by a native oxide on Si(100).

In this case, clear Si and SiO_2 peaks can be observed at binding energies of ~99 and ~103 eV, respectively. However, when the identical XPS experiment was performed on the Si(100)-2×1:H surface following 24 h of exposure to ambient conditions, no oxide peak was detected. The top trace of Fig. 1 illustrates that a faint oxide signal only became apparent after 40 h of ambient exposure. The small magnitude of this oxide peak compared to the native oxide sample suggests that the oxidation is still at the submonolayer level.

Within the detection limits of XPS, the Si(100)-2×1:H surface appears unperturbed by ambient conditions for periods up to 40 h. Consequently, a more sensitive detection technique is required to determine the surface quality following shorter exposure times. With its atomic resolution imaging capabilities, UHV-STM experiments were performed to supplement the initial XPS data. STM imaging was accomplished with electrochemically etched W and PtIr tips using a homemade microscope.[15] Prior to ambient exposure, the quality of the *in situ* prepared Si(100)-2×1:H surface was verified with STM imaging, as shown in Fig. 2(a). The surface is uniformly passivated with only a few atomic-level defects in a $(300\ \text{Å})^2$ area. The sample was then taken out of the UHV chamber and exposed to ambient conditions for 15 min. Reintroduction to the UHV STM was accomplished through a load lock that can be pumped from 1 atm to 10^{-6} Torr in ~5 min. In the UHV chamber, the sample was degassed at ~250 °C in an effort to remove any physisorbed species from the surface. Following this procedure, STM imaging [Fig. 2(b)] reveals that the hydrogen-passivated surface remains intact. Although the surface now possesses sporadic atomic-scale contamination, dimer rows and atomic steps are still clearly evident. In terms of surface flatness and cleanliness, this result notably exceeds previous STM results gathered on wet chemically H-passivated Si(100).[16–19]

The scattered contamination of Fig. 2(b) is reminiscent

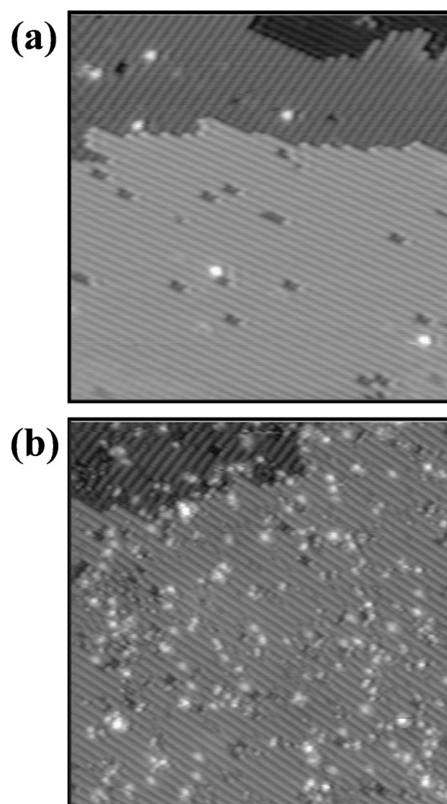

FIG. 2. Two 300 Å×300 Å STM images were taken at −2 V sample bias and 0.1 nA tunneling current. (a) This image illustrates a representative region of the Si(100)-2×1:H surface prior to ambient exposure. (b) With no precautions taken to shield the surface during pump down, the silicon dimer rows are still visible in STM images following 15 min of ambient exposure. However, spurious defects (defect density $\approx 3\times10^{13}\ \text{cm}^{-2}$) are also apparent.

of STM images performed on wet chemically passivated Si(111).[20] Since atomically pristine wet-chemical passivation recipes exist for Si(111), the presence of contamination in STM images has been attributed to the sample loading process. In particular, during the load-lock evacuation process, the pressure moves through a regime where the surface is exposed to a significant flux of kinetically energetic free radicals. In an effort to minimize surface damage in this regime, the experiment described in Fig. 2 was repeated with a ceramic shield installed on the Si(100)-2×1:H sample during load-lock venting and evacuation. The shield was mounted and removed *in situ* and only made loose contact with the sample surface. Figure 3 illustrates the Si(100)-2×1:H surface following exposure to 15 min of ambient conditions with the shield installed. Unlike Fig. 2(b), no contamination is detected in the resulting STM images. When appropriate precautions are taken during venting and pump down, the Si(100)-2×1:H surface remains atomically pristine following limited ambient exposure.

In previous STM studies, atomically flat regions of the Si(111)-1×1:H surface have shown comparable stability in ambient conditions.[20] On the other hand, STM images of dihydride Si(100) surfaces following ambient exposure have revealed high densities of atomic steps and contamination.[16–19] In all of these studies, the observed surface quality improves as the chemical uniformity and atomic flatness of the hydrogen passivation increases. By minimizing defect sites, highly uniform and flat hydrogen-passivated

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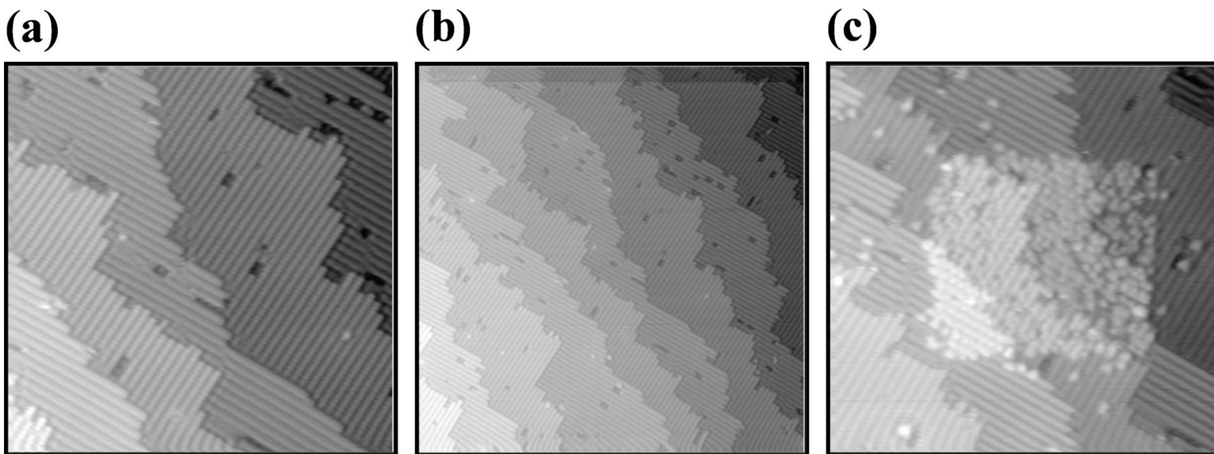

FIG. 3. Three STM images were taken at −2 V sample bias and 0.1 nA tunneling current. The Si(100)-2×1:H surface was exposed to atmospheric conditions for 15 min and protected with a ceramic shield during venting and pump down. (a) A 300 Å×300 Å STM image and (b) a 600 Å×600 Å STM image illustrate the atomic-level purity of the surface following ambient exposure. (c) A depassivated square was produced by STM-induced desorption of hydrogen to demonstrate the suitability of this surface for nanofabrication even after ambient exposure.

silicon surfaces delay the onset of nucleation and growth of contamination. In this work, the *in situ* preparation of the Si(100)-2×1:H surface has been optimized to the point where essentially every silicon dangling bond has been terminated with a single hydrogen atom, as observed in Fig. 3. The observed stability in this letter likely results from the nearly perfect chemical uniformity and atomic flatness of the monohydride Si(100) surface.

In summary, the robustness of the *in situ* hydrogen-passivated Si(100) surface has been studied with XPS and STM. XPS results show that the monolayer H passivation can prevent detectable oxidation for 40 h in ambient conditions. STM images provide atomic-level information about the initial stages of contamination. When shielding is applied to prevent line-of-sight bombardment of the surface with kinetically energetic free radicals during load-lock evacuation, the Si(100)-2×1:H surface remains atomically perfect following 15 min of ambient exposure. This robustness is potentially useful for applications that require atomically clean Si(100) surfaces (e.g., microelectronics, MBE, etc.). In addition, the results of this letter have significant implications for silicon-based nanofabrication. Figure 3(c) illustrates that STM-induced electron-stimulated desorption[3] can be used to create depassivated areas on the Si(100)-2×1:H surface. The chemical contrast between clean and H-passivated Si(100) has been previously utilized to perform nanoscale-selective chemistry in UHV.[21] Since the Si(100)-2×1:H surface has now been shown to be stable against ambient conditions, *ex situ* processing should also be possible on STM-patterned Si surfaces. The ability to combine nanolithography with ambient processing opens up opportunities for nanoscale chemical and biological applications.

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