Laser Desorption from and Reconstruction on Si(100) Surfaces Studied by Scanning Tunneling Microscopy

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Laser irradiated Si(100) surfaces were studied with an ultrahigh-vacuum scanning tunneling microscopy (STM) system. Our observations indicate that only the dimerized outermost atomic layer is removed if the laser fluence is below the melting threshold with a photon energy larger than the band gap. The newly exposed layer, surprisingly, did not have a dimerized atomic structure, but rather, resembled that of a bulk-terminated structure. The uncovered layer remained atomically smooth (no vacancies) even after 90% of the outermost layer was removed. A possible explanation of these observations is that atom removal occurs by a preferential breakage of the atomic bonds in defect sites. When the laser fluence was increased to levels above the melting threshold, extensive surface roughening occurs.
1. Introduction

1.1 Selective Laser desorption

Control of semiconductor surface morphology is an important technological goal as electronic devices approach the nanoscale size regime. Extensive research has been carried out using both growth and removal techniques. This research has included the use of laser irradiation, but generally without localization of the energy to specific sites. If a laser fluence is high, the energy deposition yields heat, plasma and related ions. Atoms and molecules can be ejected by thermal vapor, ion-sputtering, and other delocalized processes. To process surfaces on the atomic scale, a technique must be found which allows the selective removal or movement of atoms.

Studies of laser-induced desorption of atoms and molecules from surfaces show that desorption originates from electronic transitions when lasers are operated under low-power conditions [1]. For semiconductors, Itoh and co-workers have measured Ga atoms desorbed from GaP surfaces [2] and Si atoms from Si(100) surfaces [3]. Their studies suggest that atom desorption occurs on defect sites during the laser irradiation at power levels below the ablation threshold.

To date, electronic laser desorption has been studied only by measuring gas-phase atoms and molecules desorbed from surfaces. The desorbed species sometime maintain a memory of the surface and provide some insight on the surface indirectly. Very few studies have been conducted by probing the fate of surfaces after irradiation. Presently, the scanning tunneling microscope operated in ultra-high vacuum provides the best tool for monitoring the surface morphology.

We studied the effects of irradiation on Si(100) surface by using an ultra-high vacuum (UHV) scanning tunneling microscope (STM) system coupled with a Nd:YAG laser (Continuum). This paper extends a previous, preliminary report [4].
1.2 Semiconductor Surface Structures

The use of new techniques to create new surface structures is providing new insights into physics at the surfaces. Recently, Salling and Lagally observed the dimerized structure in the second layer after removing dimers in the first layer by means of a voltage-pulsed STM tip [5]. Our preliminary results [4] show that the second layer structure is altered from that of the thermally annealed surface and is similar to the bulk-terminated structure after removal of part of the first layer by laser irradiation. These data may suggest that the structure of the second layer of the Si(100) surfaces depends upon the process by which the atoms in the first layer are removed.

For many years there have been many theoretical efforts to reveal the atomic structure of the underlying layer as dimers are removed from the Si(100)-2x1 surfaces. Pandey predicted that upon removal of surface dimers, the atoms beneath the vacancies would bond together to form new dimers [6]. Contrary to Pandey's prediction, Roberts and Needs' calculations show an energy cost to re-bond after dimer removal [7]. But neither of these results provide support for a bulk-terminated structure of the layer beneath surface vacancies.

The static structures of Si(100) surfaces are expected to be influenced by the existence of adsorbates and/or vacancies. It is well known that the 2x1 reconstruction characteristic of the clean surface is changed by adsorption of impurities such as H$_2$ [8] and H$_2$O [9]. This relaxation is a result of extraction of electrons from the dimer bonds by the impurity which saturates the surface dangling bonds. The Si(100) surface can also form 2x6, 4x8, 4x4, and 1x5 reconstructions with Sn atoms present on the surface, depending on Sn coverage [10], 2x2 for In presence [11], 2x3 for Ag coverage [12], and 4x4 for boron [13].

2. Experimental

Experiments were carried out in an ultra-high vacuum (UHV) chamber, equipped with STM (Omicron) and coupled with a pulsed Nd:YAG laser. Most images were acquired in the constant current mode using tunneling currents of 0.2-0.6 nA and sample bias between -1.5 and -3.0 V. The scan rate was typically 500 μs per point with image resolutions of 400 points
by 400 points. Calibration of the x, y and z piezo drives was made from measurement of the lattice distances and single step heights of Si(100)-2x1 and Si(111)-7x7 surfaces.

The Si(100) samples used in these measurements were cut from a polished p-type wafer (6x3x0.2 mm) with less than 1 ohm/cm resistivity. The sample was clamped on a mounting stage made of molybdenum and tantalum. The silicon sample was cleaned in an ethanol ultrasonic bath before being transferred into the UHV chamber. After outgassing at 775 K overnight, the sample was flashed to 1425-1475 K for 1-2 minutes and then slowly cooled to room temperature at the rate of about 1 K/sec, although the cooling rate was not found to be critical. Images were acquired at room temperature.

After processing and characterizing a clean, well-reconstructed Si(100) surface, the sample was irradiated by a single or multiple pulses of a frequency doubled, pulsed Nd:YAG laser (532 nm wavelength, 7 ns pulse width). The laser light is delivered to the sample through a pyrex window after passing a set of apertures, which limit the beam diameter on the sample to about 3 mm. Laser power was altered with Q switch delay and was measured using a diode power meter.

3. Results

3.1 Thermally annealed Si(100) surfaces

Symmetric dimers appear in Fig. 1a as elliptically-shaped protrusions with minor axes aligned along the dimer row direction, i.e. perpendicular to the dimer bond direction. It is believed that dimerization involves recombining the four dangling bonds of two adjacent surface atoms into occupied σ and π orbitals [14], accompanied by a decrease in the spacing between the dimer pairs, compared to the ideal termination. The electron distribution in the occupied π states is maximal in the center of the dimer. The STM image mainly reflects the π electrons under these conditions. It is believed that dimers buckle into two directions, separated by an energy barrier that is comparable to thermal energy at 120 K [15]. Hence, the dimers fluctuate on a time scale that is small compared to the imaging time and they appear to
be symmetric. Zig-zag dimers are observed near defects or at the edges of steps. This is believed to be elastic strain and Coulomb potential interactions.

Figure 1(b) shows STM images of un-occupied states of a reconstructed Si(100)-2x1 surface. The image in Figure 1(a) was taken with a +3 volt sample bias and 0.6 nA tunneling current. Clearly, the image is atomically resolved in both perpendicular and parallel directions to the dimer rows. Spacing in the parallel direction is 3.84 Å, equal to the surface lattice constant. The ability to resolve silicon atoms in the un-occupied state is understood to be due to decreased electron density at the center of the unoccupied π orbital of the Si-Si bond compared to the filled π orbital [8].

The STM image in Fig. 1(a) also shows marked clustering and alignment of vacancies in the outermost layer, shown as dark patches, as well as randomly distributed dimer vacancies in the outermost layer. Ordering of vacancies into 2xn periodicities (where n≈10) is consistent with previous measurements [16]. In some work, the 2xn vacancies are attributed to Ni impurity presence on the surface [17]. It appears that such vacancies cannot be avoided on the dimerized Si(100) surface when the surface is annealed around 775 K and flashed below 1,475 K. We found that higher temperatures can reduce such defects, but cause surface roughening, evident from high quantities of steps and random orientation.

It is useful to point out that after annealing a Si(100) surface above 1,250 K, we observed no effect of cooling rate on the clean Si(100) 2x1 images. Traditional wisdom requires that the "cooling rate should be slow at a rate of <20/s from 1,250 K to room temperature." [18] We cut off the heating current (directly through the sample) immediately from 1,250 K. The pyrometer indicates that the surface cools down to <500 K within two seconds. After these events, STM images appear similar to those obtained via the slow cooling processes.

3.2 Dependence upon Laser Power

The initial Si(100) surface was irradiated by the laser with varying fluence. Figure 2(a)
shows the occupied-state STM image of a Si(100) surface irradiated by one laser pulse with a fluence estimated to be 150 mJ/cm². For a 7 ns pulse width at the wavelength used, the melt threshold is about 250 mJ/cm², as calculated from a formula provided in reference [19], while the ablation threshold is about 1.0 J/cm². In contrast to the images of the thermally annealed surface (Fig. 1(b)), larger dark patches appear in the outermost layer after the laser irradiation.

The apparent height between the top layer dimers and the dark patches was measured, as shown in Figure 3. The normal step height of 1.36 Å measured on thermally annealed Si(100) was used to calibrate the z scale (Fig. 3a). The height of the top of the dimer layer above the dark patches is measured to be 1.64 Å (Fig. 3b), assuming a simple topographic interpretation of the images. Hamers et. al. observed another kind of dark site which appears 0.8 Å lower than the normal dimer. They attributed the dark sites to electronic differences in the H-Si sites, not vacancies [8]. The 1.64 Å apparent step produced by laser irradiation is larger than that of Si-H sites. As described later, the number of the dark patches are linked to the yield of silicon atoms laser-desorbed from Si(100) surfaces [3]. Based on these data, we conclude that the dark patches are vacancy islands produced by the laser.

Figure 2(b) shows a STM image after one laser shot at a fluence of about 300 mJ/cm², which is above the melt threshold. Other laser conditions were held the same. The original flat surface becomes roughened, indicating laser damage to multiple layers. Similar multilayer damage was reported by Wiesendanger et. al. on STM studies of laser- and thermal-annealed Si(111) surfaces [20] with a laser fluence above the ablation threshold. Their images show that the surface is disordered after the anneal. In contrast, the Si(100) surfaces irradiated with the power used in this work still keeps the 2x1 reconstruction, although it is damaged on a larger scale. Many factors may contribute to this difference. For example, the laser processing was followed by thermal anneal before imaging in their experiments, while STM images were taken immediately following the irradiation in this work.
3.3 Dependence upon the Number of Laser Pulses

Maintaining the laser fluence in which only the outermost layer is removed, as shown in Fig. 2a, the number of laser pulses was increased. The time separation between the pulses is greater than 0.5 s, allowing the surface to return approximately to room temperature between pulses. Fig. 4a and 4b show the images after 17 and 37 pulses, respectively. The fraction of the surface appearing as dark patches (vacancy islands) increases with the number of pulses, occupying about 60% and 90% of the surface after 17 and 37 pulses, respectively. Comparing Fig. 4a with Fig. 2a, the concentration of dimer rows becomes a minority, but they are still clearly seen as outlined in the box. Apparently, only 10% of the original outermost Si layer remains as the bright spots shown in Fig. 4b for 37 pulse irradiation. Since the remaining dimers concentration is so small, no clear dimer rows are observed.

Various images with intermediate quantities of vacancies were obtained for intermediate numbers of the laser pulses, and the fraction of the dark patches (v) were counted as a function of laser shots. Then the fraction of the surface covered by the remaining dimers is reasonably assumed to be (1-v). Figure 5 plots the remaining dimer fraction as a function of the number of laser pulses. The dimer concentration decreases as function of the pulse number. The curve in Fig. 5 is a single exponential function, which, clearly, cannot fit the data.

In experiments performed by Kanasaki et. al. [3], the yield of Si atoms laser-desorbed from Si(100) surfaces was measured. Their results indicate that for fluences in the range of 220 to 510 mJ/cm², the desorption yield rapidly decreases as the number of laser pulses increases. As in previous experiments on GaP and GaAs, they conclude that this rapid desorption arises from Si adatoms or Si atoms associated with surface defects. For their experiments using a 500 nm excimer-pumped dye laser and pulse width of 28 ns, the melt threshold is about 500 mJ/cm². In the present experiments the formation of the dark patches in the STM images occurs at fluences also below the melt threshold. The observed decay of the top layer dimer density is linked to the decay in the desorption rate of silicon atoms from Si(100) surfaces. This correlation between the gas phase atoms and the remaining surface
confirms that the dark patches are vacancies left after removal of the top layer dimers.

Note that vacancies are not introduced into the uncovered layer by multiple laser pulses, as shown in Fig. 4b. If laser removal occurred layer-by-layer, the new top layer should also be affected. However, laser removal ceases at the uncovered layer (for up to 90% of dimer layer removed) unless the laser power is increased above the melt threshold. This suggests that laser removal may be sensitive to in-plane vacancies or dimerization. The initial dimerized layer has many vacancies while the uncovered layer has none. Also the initial top layer is fully dimerized while the uncovered layer is not.

3.3 New Structures of Si(100) Surfaces

Figure 6 expands the image shown in Fig. 2a. The Si atoms in the top layer remain in dimer rows. The image of the occupied states for the underlying, "uncovered" layer is atomically resolved. Two small, broken rows are seen which are within a space of 7.7 Å in the <10> direction. For a thermally annealed 2x1 surface, only one dimer row was observed in this space. Fig. 7b plots the corrugation of this layer as a function of the distance along the <10> direction, perpendicular to the direction of the dimer rows. A least squares fit shows a fundamental distance of 3.83 Å, which is equal within experimental error to the inter-atom spacing (3.84 Å) in bulk Si(100) planes. Assuming the STM image reflects nuclear positions, these data imply that the uncovered layer has the bulk terminated 1x1 configuration for small fractions of missing dimers, while dimerization in the first layer remains.

Figs. 7c and 7d show the heights measured in the second layer as a function of distance along a <10> atomic row, for the surfaces in which 60% and 90%, respectively, of the dimerized layer have been removed. We fit the height curves to periodic functions with 7.7 Å as the periodic length for each two small rows and a variable distance for the length between the two rows. The least squares fit shows that distances between the closest atoms in the uncovered layer are 3.6 Å and 3.4 Å for the surface with 60% and 90% vacancies,
respectively. These distances appear to decrease slightly as the fraction of missing dimers increases. However, the spacings are considerably larger than the commonly accepted dimer spacing of 2.4 Å, which suggests that the uncovered surface is not dimerized as shown in the thermally annealed surface. Our data suggest that both the electronic and geometric structures of the layer uncovered by laser irradiation are different from those of the thermally annealed surfaces.

Fig. 4a show a slight pairing in the second layer in the same direction as the pairing in the top layer. This might suggest that two Si layers are removed at the dark patches. We believe that this is not the case since the measured height of 1.64 Å is closer to the single layer height, 1.36 Å, than that of a double-layer, 2.72 Å.

4. Discussion

4.1 Mechanisms responsible for selective desorption

Laser irradiation with the fluence used (150 mJ/cm²) increases the temperature in the heat diffusion-length layer to about 775 K. At this temperature, thermal desorption does not contribute to the top-layer dimer removal, so the possibility of desorption induced by electronic transitions (DIET) must be taken into account [21]. For electronic processes, the ease of extraction of an atom is determined by the specific local bonding configuration.

The left side of Fig. 8 illustrates a model of dimers with a vacancy presence in the outermost layer of Si(100) surfaces after thermal cleaning. The right side schematically shows the density of state diagram for bulk silicon and for Si(100) reconstructed surfaces. The dished line illustrates surface vacancy states located in the band gap.

Laser irradiation deposits the energy into the near-surface bulk in the range of 0.5 μm (Step I). Initially very little energy is deposited to the top layer. Holes are generated in the bulk due to the excitations of electrons from the bulk valance band to the conduction band, probably also to the unoccupied surface states. Some of these holes diffuse to the surface and may be trapped at the surface vacancies (Step II). Atoms near the vacancies initially are in
bonding states. After trapping the hole, the bond of the atom is weakened. Continued laser radiation during the pulse period forms an additional hole or more. The atom trapping the multi-holes will be in antibonding states and consequently ejects from the surface. We don't think that a single-hole state is an antibonding state since no linear relation between the laser fluence and desorption yield is shown in present literatures [22].

This model indicates that the presence of vacancies is required for silicon atom desorption under sub-threshold laser irradiation. For the outermost layer which normally contains vacancies, atoms in the layer will be removed by the laser irradiation. For the uncovered layer, vacancies are not observed, so this layer is not affected by the laser irradiation.

4.2 Reconstruction of Laser Irradiated Si(100) Surfaces

For the dimerized reconstruction of Si(100) 2x1 surfaces, the direction of the dimer bonds in a layer is perpendicular to that of the next layer separated by a single-atom step. The conventional dimerization includes both formation of π and σ bonds by pairing the dangling electrons and moving two atoms together. In this work, the direction of the slight pairing in the laser-uncovered layer tends to be parallel to that of the outermost-layer dimer bond. Since we rule out of the possibility of double layer removal, the slight pairing may not be the dimerization.

It is well known that the 2x1 reconstruction characteristic of the clean surface is changed by adsorption of impurities such as H₂ [8] and H₂O [9]. Is it possible that the (1x1) structure observed in the un-covered layer results from islands of impurities resulting from ambient gas exposure during the laser anneal process? We rule out this possibility based upon the following reasons. First, the step height at the edges of the dark patches is close to that expected for a clean surface. The step height measured in Fig. 3, is 1.64 Å compared to a single-layer step height of 1.36 Å observed for clean Si(100) surfaces. An exact single-layer step height would not be expected if the electronic structures in the two layers were different.
For a Si(100) surface with islands of adsorbed hydrogen, Hamers et al. measured an apparent 0.8 Å height difference between H islands and clean Si dimers [8], in contrast to the present case. Second, the concentration of the remaining dimers correlates to that of silicon atoms desorbed from the surface as described above. Finally, a control experiment was performed in which the sample was transferred into and held in the side-chamber used for laser processing but without actual irradiation. Following this procedure the sample maintained the 2x1 structure characteristic of the clean surface.

Another caveat is that surface impurities originate from the bulk due to surface segregation induced by the rapid laser anneal. A likely possibility is boron, present as a p-type dopant in the Si. This possibility is eliminated for the following reasons. Recent results obtained by Wang et al. [13] show that the presence of 0.5 ML of boron induces 4x4 reconstructions on Si(100). No trace of such reconstructions were observed following laser irradiation. Furthermore, the laser anneals were preceded by lengthy thermal anneals in which the temperature was higher than the peak temperatures achieved during the laser pulse. Any surface segregation should already have occurred, but apparently did not since the STM images are those characteristic of a clean surface. Previous studies of laser induced surface segregation involved power levels above the melt threshold where impurities are thrust to the surface by a retreating melt front [19]. Since the laser power in the present case was below the melt threshold this mechanism is not applicable. Finally, re-annealing the laser irradiated surface returns it to the 2x1 structure, indicating that there are no strongly bonded surface impurities.

We believe that the bulk-like 1x1 structure observed in the uncovered layer, for 20% removal of the dimer layer, is due to non-equilibrium metastable states associated with the presence of the remaining top dimer layer and the absence of vacancies in the uncovered layer. As pointed out by Roberts and Needs [7], re-bonding of two atoms beneath a dimer vacancy is inhibited by increased lattice strain energy. For a small fraction of dimers removed by laser irradiation, the strain prevents such re-bonding, tending to keep the surface unreconstructed.
For larger fractions, the strain energy is reduced. Evidently, reduction in strain is manifested as a decreased pairing distance, observed when larger fractions of the dimer layer are removed. In the study of Salling and Lagally [5] in which the exposed second layer is dimerized following removal of first layer atoms with a pulsed threshold voltage applied to the tip, atoms are removed from multi-layers even at voltages slightly above the threshold. Since the voltage-pulsed tip is able to remove atoms from the second and third layers, we believe that it could also assist the dimerization.

5. Conclusion

In summary, laser irradiation of Si(100)-2x1 at a fluence below the melt threshold selectively removes the dimerized outermost layer of the surface. The layer un-covered by the laser appears to have a bulk-terminated 1x1 structure for small fractions of the dimer layer removed and a distinct new 2x1 structure with larger fractions. Continued laser irradiation at this fluence does not introduce vacancies into the uncovered layer. Electronic laser desorption initiated at surface vacancies is suggested to be responsible for such a selective process. The data reported here suggest that future developments could result in a method for producing atomically smooth silicon surfaces by selectively peeling away dimers or atoms adjacent to vacancies, leaving a defect-free surface.

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References:


Figure captions:

Figure 1. STM images of thermally annealed Si(100)-2x1 surfaces (200x200 Å). (a) Occupied states with -3 V sample bias and 0.6 nA of the tunneling current, (b) Unoccupied states with 3 V sample bias and 0.6 nA of the tunneling current.

Figure 2. STM images of Si(100) as a function of laser fluence (200x200 Å). (a) one laser shot with 350 μsec Q-switch delay, estimated laser fluence of 150 mJ/cm², (b) one laser shot with 250 μsec Q-switch delay, estimated laser fluence of 300 mJ/cm².

Figure 3. Apparent heights (a) for a normal Si(100)-2x1 step and (b) for laser-induced dark patches.

Figure 4. STM images of a Si(100) surface as a function of the number of laser shots (100x100 Å): (a) 17 shots and (b) 37 shots. The laser fluence is maintained about 150 mJ/cm², which is below the melt threshold of Si(100). The sample bias is -3 Volts and the tunneling current is 0.6 nA for all images.

Figure 5. Plot of the remaining dimer concentration of laser-irradiated Si(100) surface as a function of the number of laser shots. The initial vacancy yield without laser irradiation has been subtracted.

Figure 6. A high resolution image of the laser-irradiated Si(100) surface (the same laser conditions as described in Fig. 2a. Clearly, the 1x1 bulk-terminated Si(100) structure is observed in the laser-uncovered layer, as seen in the outlined box.

Figure 7. Height profiles of the second layers measured along <10> direction, perpendicular to the dimer row direction for (a) un-irradiated, (b) 1 pulse, (c)17 pulses, and (d) 37 pulses of laser irradiation of Si(100) surfaces.

Figure 8. Left: schematic representation of a dimerized Si(100) surface with a dimer vacancy. Right: schematic diagram of the bulk, surface, and defect band structure for Si (100) surfaces. Step (I) indicates formation of an electron-hole pair via laser excitation of an electron from the bulk valance band to the bulk conduction band or to the surface un-occupied band. Step (II) indicates migration of the hole to the surface and being trapped in the vacancy band.