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Structural changes caused by H_2 adsorption on the Si(111)7 × 7 surface

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Structural changes caused by the adsorption of molecular hydrogen adsorption onto the Si(111)7 × 7 surface reconstruction are quantified using the first structure parameter refinement on transmission electron diffraction (TED) data. We find that initial adsorption of molecular hydrogen onto the Si(111)7 × 7 surface causes a preferential decrease in the occupancy of the center adatoms. Further adsorption of hydrogen results in the breaking of the dimer bonds and the removal of the corner adatoms.

Quantitative structural studies of surface/gas reactions have heretofore been difficult because they generally require real time diagnostics and measurement at elevated temperature. A technologically important example is hydrogen adsorption on silicon. The adsorption of *atomic* hydrogen onto clean silicon surfaces has been well studied at room temperature [1–18], conflicting information exists for the adsorption of molecular hydrogen onto clean silicon surfaces [1,7,11,12,19] and little is known about the adsorption of either atomic or molecular hydrogen on silicon surfaces at elevated temperature. Numerous studies have been made on the Si(111)7 × 7 : H surface including: low energy electron diffraction (LEED) [1,10–12,15], reflection high energy electron diffraction (RHEED) [17], ion-channeling [11], high-resolution IR [13], high-resolution electron energy loss spectroscopy (HREELS) [9], and scanning tunneling microscopy (STM) [18], but the structure of the Si(111)7 × 7 : H remains unclear. In a paramagnetic resonance study, H_2 was found to adsorb onto crushed silicon in a thermally activated process, and the adsorbate was thought to be molecular [19]. Ibach and Rowe, in a LEED study [1], reported that H_2 adsorbed only in small quantities – 3% surface coverage, and interpreted this coverage to relate to defect density. In an EELS study, Froitzheim et al. [7] reported a sticking coefficient of unity for molecular hydrogen adsorption at room temperature on the Si(111)-2 × 1 surface and a vibrational loss peak of 100 meV which was attributed to a hydrogen atom bonded between two silicon atoms at a step edge. Culbertson et al. [11] also noted that vibrationally excited molecular hydrogen might dissociatively chemisorb onto the Si(111)7 × 7 surface at room temperature. In a LEED study [12], Schulze and Henzler reported that H_2 did not affect the structure of the Si(111)7 × 7 surface. They also reported that the desorption peak maximum for the hydrogen-covered Si(111) surface in vacuum is 520°C.

We use the first structure parameter refinement on transmission electron diffraction (TED) data and show that initial molecular hydrogen adsorption on the Si(111)7 × 7 surface results in a preferential decrease in the center adatom occupancy over other sites already at room temperature. Further adsorption results in the breaking of the dimer bonds and the removal of the corner adatoms.

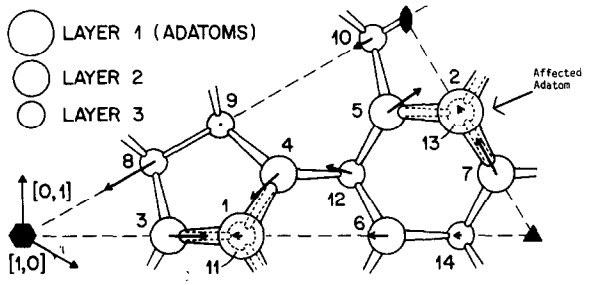

Fig. 1. Atomic model and numbering scheme of the crystallographic asymmetric unit of the Si(111)7×7 unit cell. The entire unit cell can be generated by applying the indicated symmetry operators. Atoms are drawn in the ideal lattice positions of the Takayanagi model. Layer A is the outermost layer. The hexagonal coordinate system is such that atom 8 is at [1,1], atom 3 is at [4/3,2/3], etc.

The atomic model of the crystallographic asymmetric unit and the numbering scheme of the Si(111)7 × 7, as proposed by Takayangi, are shown in fig. 1. As can be seen in fig. 1, the Si(111)7 × 7 offers several sites for reactive adsorption of hydrogen. Possible adsorption sites include the dimer bonds 8–9 and 10–10′, the rest atom 6, the corner adatom 1, and the center adatom 2.

We use transmission electron diffraction (TED) because the diffraction of high-energy electrons by surfaces is efficient, permitting pattern collection in seconds, yet weak enough to allow kinematical interpretation. It is therefore complementary to scanning tunneling microscopy (STM), which studies only the top layer of a solid, and to highly dynamical electron diffraction techniques such as RHEED, or LEED. The efficient scattering of high-energy electrons, in comparison to X-rays, is particularly important for dynamical studies where real time data collection is needed. We evaluate our TED data for the first time by a combination of structure parameters refinement – a technique employed in analyzing quantitative X-ray diffraction data, and difference Fourier maps.

We conducted our experiments in a modified JEOL 200CX transmission electron microscope [20] at an electron accelerating voltage of 100 keV. The specimen sits inside the microscope in an ultra-high vacuum chamber with a base pressure on the order of 1×10^{-9} Torr. All Si(111) samples were 10 Ω · cm p-type disks with a chemically etched hole in the center. The specimens were heated in-situ at 1200°C to produce thin (< 1000 Å) 1 μm^2 areas, and then flash cleaned at 1200°C for several seconds. From an earlier analysis of the intensity and peak shape of the surface termination (1,0) spots [21], we showed that this technique produces flat areas with an upper limit to the surface step spacing of > 1000 Å. All hot filament gauges inside the vacuum chamber were turned off during the adsorption experiments. The pressure of H_2 (99.9995%) was monitored by a residual gas analyzer 30 cm from the sample and not in line of sight. That also was turned off for several experiments and no change in the rate of H_2 adsorption was detected. The sample was heated by direct passage of current and the temperature calculated from the power dissapation to ±50°C accuracy (calibrated with an optical pyrometer). Diffraction patterns were taken at temperatures, pressures, and H_2 exposure times as noted. All diffraction data were reproducible. We conducted extensive experiments to separate the effect of the high energy electron beam from the experimental results. These included experiments with the beam on during hydrogen dosing, beam off during hydrogen dosing, and experiments in a separate vacuum chamber using low energy electron diffraction (LEED) – which will be discussed later in the text. An effect of the high energy electron beam on the diffraction data was found only for beam exposure times > 3 min [22]. The data reported herein was taken with the beam off during hydrogen dosing, and beam exposure times < 1 min. Diffraction patterns were recorded by direct exposure of the electron beam onto a photographic plate in the linear response region of the emulsion. Negatives were digitized using a linear photodiode array. The background was subtracted from the integrated peak intensities. At least three symmetry equivalents of each diffracted beam were averaged together; they had an uncertainty determined by reproducibility which was 13% on average. Typically 400 beams were measured, reducing to 60 inequivalent beams after averaging.

Starting with the dimer adatom stacking fault (DAS) model [23] for the 7 × 7 surface, and using refined coordinated [24] we have used a least-squares method of refinement to solve for the coordinates of all fourteen atoms in the Si(111)-

Table 1
Structural solutions of a parameters refinement made on the digitized diffraction patterns of a temperature and dose series (the 500 °C 'No H_2' data was taken after ten minutes at 500 °C in vacuum)

Temperature (°C)	H_2 dose (L)	χ^2	R	Adatom 1 Occup.	Adatom 2 Occup.	Dimer 8–9 (Å)	Dimer 10–10′ (Å)
RT	2400	3.8	0.18	100	41	2.4	2.6
350	2400	3.8	0.18	100	26	2.5	2.7
500	No H_2	3.5	0.16	100	75	2.3	2.6
500	720	4.0	0.20	100	54	2.3	2.5
500	1440	4.3	0.25	100	41	2.3	2.5
500	2400	3.9	0.17	99	24	2.4	2.5
700	2400	4.1	0.23	64	16	2.6	2.9
800	2400	2.7	0.15	100	54	2.4	2.6

7×7 : H unit cell. We kept the 6 mm point symmetry of the original structure, leaving 17 positional parameters for the 14 atoms of the asymmetric unit. Of these, 15 parameters could be refined satisfactorily; separate displacements for the two adatoms (1 and 2 in fig. 1) and the third layer atoms immediately below (11 and 13) could not be assigned in projection, so these were allowed to move in parallel as two pairs. The Debye–Waller factors were fixed at 1.5 Å^2 for the top layer atoms, and 1.4 Å^2 for the atoms in the two layers below. A scale factor for the data was refined along with the 15 structural parameters. Two additional parameters, the occupancies of the adatoms 1 and 2, were also refined. To validate the results, isolated parameters, such as the adatom

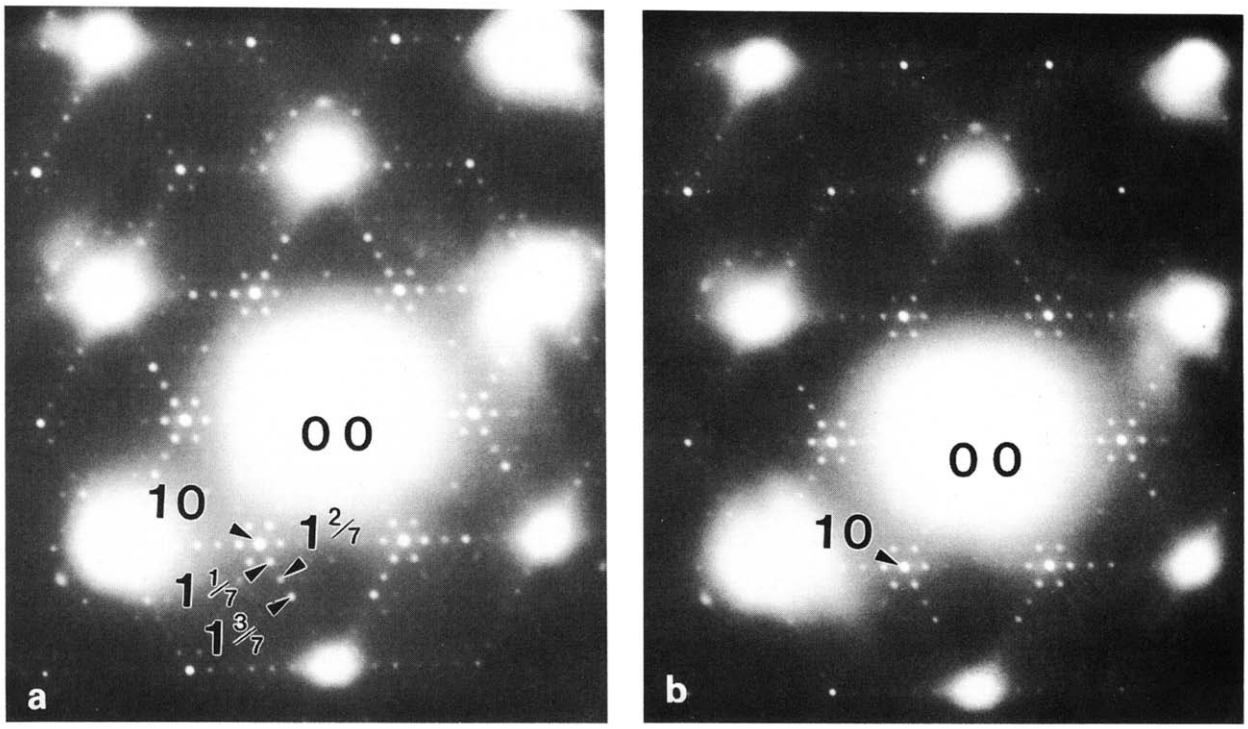

Fig. 2. Transmission electron diffraction patterns (a) of the clean Si(111)7 × 7 surface and (b) after 2400 L exposure to H_2 using 100 keV electrons. The sample temperature was 500 °C and the hydrogen pressure was 4×10^{-6} Torr.

occupancies, were also refined while all other parameters were held constant. All refinements yielded fits with a least-squares residual [25], chi-square < 4.4 and an unweighted R [26] of < 2.6. For example, the data after hydrogen dosing at 500°C yielded an unrefined chi-square fit of 13.8 to the clean surface at 500°C. After full structural refinement we found a stable chi-square fit of 3.9. Refining all parameters (including the Debye–Waller factors), but keeping the adatom occupancies fixed at the clean surface values, gave a chi-square fit of 9.6. A refinement of just the adatom occupancies with all other parameters fixed at the clean surface values, gave a stable chi-square fit of 4.5. A detailed discussion of the structural refinement procedure as well as a listing of the diffraction data will be published elsewhere.

Transmission electron diffraction patterns of the Si(111)7 × 7 surface before and after exposure to 2400 L of H_2 (4×10^{-6} Torr) at 500°C are shown in fig. 2. We see that after H_2 exposure (fig. 2b), the (1,3/7 and (1,4/7) diffracted beams have decreased in intensity relative to the (1,1/7) beams. We chose one representative temperature and dose series for the structure parameters refinement, and the results are shown in table 1.

The initial structural change caused by H_2 adsorption on the Si(111)7 × 7 surface is a decrease in the occupancy of the center adatom 2 (fig. 1). At room temperature, after exposure of 2400 L of H_2, the occupancy decreases from the clean surface value of 92% to 41%. For elevated temperatures, the occupancy of adatom 2 is sensitive to temperature as well as hydrogen exposure. For the clean surface held for ten minutes at 500°C, the occupancy of adatom 2 decreases from 92% to 75%. After 720 L of H_2 at 500°C the adatom 2 occupancy decreases from 92% to 54%, after 1440 L to 41% and after 2400 L to 24%. Below 700°C, we observe little effect on the dimer bonds or on adatom 1.

At 700°C, we observe a decrease by a factor of two on average in all fractional order beams after a 2400 L dose of H_2. In table 1 we see that the occupancy of adatom 2 is down to 16%, and that the occupancy of adatom 1 is also decreased to 64%. Both dimer bond lengths have increased (the bond length is most likely an average between those that have completely relaxed and those that are still dimerized). At 800°C, just below the transition temperature at which the 7 × 7 converts to a 1 × 1 structure, the diffraction pattern does not appear to have changed after an H_2 dose of 2400 L. A chi-square fit of 3.9 to the clean surface was obtained.

We have made difference Fourier maps to further validate the results of the structural refinements. Whereas structure parameters refinement is non-unique, and works only for small structural perturbations from a model, the only assumption for a difference Fourier map is that the structure factor phases are relatively unaffected by hydrogen exposure [29]. A representative difference map taken between the digitized data set before and after exposure to 2400 L of H_2 at 500°C (fig. 2) is shown in fig. 3. We see that the most pronounced

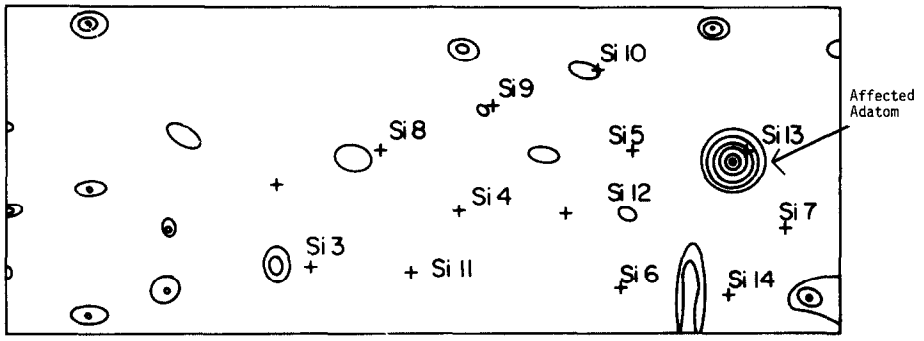

Fig. 3. Difference Fourier map of the crystallographic asymmetric unit of the 7 × 7 unit cell (fig. 1) taken between digitized data sets before and after exposure to 2400 L of H_2 at 500°C (the two diffraction patterns of fig. 2). The phases were derived from the refined clean surface. Equally spaced positive contours are drawn, the lowest being omitted for clarity.

feature is a hole at the position of the center adatom 2 confirming the results of the structural refinement.

We found that annealing to 800°C for several seconds was not enough to recover the full adatom 2 occupancy after dosing with 2400 L of H_2 at 500°C. Rather, an anneal to 1000°C was required. Since hydrogen desorbs from silicon surfaces well below 800°C [12] the surface does not appear to reconstruct concurrently with hydrogen desorption. The affected adatoms may have been completely removed as SiH_4 or SiH_x, a mechanism supported by the earlier HREELS study which reported SiH_4 desorption after atomic hydrogen exposure to the Si(111)7 × 7 surface [14]. The high temperature anneal then would be needed to resupply adatoms by silicon diffusion from steps.

STM studies of the adsorption of NH_3 [27] and Cl [28] on Si(111)7 × 7 also found that the center adatom was more reactive than the corner adatom. Robinson et al. [24] and Payne [29] have shown by qualitative strain arguments that the adatom bonds are strengthened by the neighboring dimer bonds, and since the center adatom is stitched by only one dimer (whereas the corner adatom is stitched by two) it could be more reactive than the corner adatom. Another explanation for a weakly bound adatom 2 is that the rest atom dangling bonds next to adatom 2 are preferentially passivated by H atoms thus transferring electronic charge back up at a rate slower than the resupply of Si atoms by diffusion from steps, so that the 7 × 7 structure is maintained, however this would not be consistent with our annealing results.

To eliminate the possibility that the high energy electron beam caused the dissociation of H_2, we conducted LEED experiments in a different vacuum chamber (base pressure – 1×10^{-11} Torr) with all hot filament gauges off. We reproduced the H_2 induced sequential structural changes which we had observed by TED. In a separate experiment on growth, we found that the Si(100)-2 × 1 surface is converted to 1 × 1 : H after 1800 L (1×10^{-5} Torr) exposure to H_2 at 650°C, and that the chemisorption of H_2 onto the Si(111)2 × 1 surface disrupts the epitaxial growth of silicon [31].

In conclusion, we have used for the first time a structure parameter refinement, and a difference Fourier map on transmission electron diffraction (TED) data to show that initial molecular hydrogen adsorption on the Si(111)7 × 7 surface results in a preferential decrease in the center adatom occupancy even at room temperature.

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