

Structure, Stability, and Origin of $(2 \times n)$ Phases on Si(100)

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Phases with $(2 \times n)$ structure ($6 < n < 10$) can be formed on Si(100) by rapid quenching from high temperatures. The nominal (2×7) phase has been investigated by high-resolution low-energy electron diffraction. The structure involves two atomic levels, is metastable, and decays with first-order kinetics. The structure can be explained by ordering of excess missing-dimer defects, which apparently are present on the surface with any of the standard surface preparation techniques for Si(100).

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The structure of the Si(100) surface continues to generate significant interest. After considerable theoretical development, it is now generally believed that the (2×1) structure that is commonly found on this surface consists either of symmetric dimers that may contain ordered defects¹ or occur in chains,² or of buckled dimers.³ Recent scanning tunneling microscopy measurements⁴ of Si(100)- (2×1) appear to confirm the dimer nature of the surface but show considerable disorder in the structure. It is also well known that Si(100)- (2×1) does not produce diffraction features that are as sharp as those on other surfaces, supporting the existence of disorder.

Other phases have been found on Si(100). A $c(4 \times 2)$ phase can be produced by particular sample-cleaning procedures and very slow cooling.⁵ Higher-order reconstructions can be produced by quenching from high temperatures.⁶ In this Letter, we report the results of a detailed diffraction study of $(2 \times n)$ phases formed on clean Si(100) by quenching from high temperatures. We find that n can vary continuously depending on the initial conditions and quench rate. In particular, we describe the nominal (2×7) structure. We show that it must consist on the average of two levels, with six units "up" and one "down" along the "7" direction. The only structure that appears to be consistent with these results is a model with ordered missing-dimer defects.¹ We determine the average sizes of the (2×1) and (2×7) domains, show that the (2×7) phase is metastable, and show that it decays with first-order kinetics. This phase can be formed with a variety of surface preparation techniques for Si(100). We suggest that Si(100) surfaces generally contain a nonequilibrium concentration of point defects.

The measurements were made in a high-resolution surface-sensitive diffractometer⁷ that has a resolving power in excess of 5×10^{-4} rad, a value that translates into maximum resolvable distances of greater than several thousand angstroms. A variety of surface-cleaning procedures were used. To produce the

$(2 \times n)$ phases, pieces of Si wafers were outgassed at 600 °C for extended periods until the background pressure returned to $\sim 3 \times 10^{-10}$ Torr and then raised to 800 °C and outgassed further if the pressure rose significantly. After a subsequent anneal for about 15 min at higher temperatures, the sample was quenched at initial rates of up to 200 °C/sec. By varying the maximum annealing temperature (950 °C to ~ 1200 °C) and quenching rate (≤ 200 °C/sec), $(2 \times n)$ phases over the range of $n = 6.5$ and $n = 9.6$ have been produced. Higher quenching rates or quenches from higher temperatures produce smaller n . Samples without at least a few minutes of annealing time above 1150 °C showed some C and O contamination, but still produced $(2 \times n)$ phases. To produce the (2×7) phase, the sample was heated to ~ 1200 °C for 2 min to remove residual C and O contamination, held at ~ 1000 °C for ~ 15 min, and then quenched. Extended heating ($\geq \frac{1}{2}$ h) above 1250 °C produced an irreversible roughening of the surface that no longer permitted formation of any $(2 \times n)$ phase. Temperatures were measured with an infrared pyrometer calibrated to a Chromel/Alumel thermocouple from 300 to 1100 °C.

In order to address the question of impurity stabilization of these phases, high-sensitivity Auger-electron spectroscopy measurements were made as a function of temperature up to 1200 °C. No impurities were found except for small concentrations of C and O at room temperature which appear to be electron-beam induced (i.e., their concentration increased with time at the point of exposure but was negligible away from this point). Special attention was paid to metallic impurities. An upper limit of 0.03% for the surface concentration of Ni was determined, based on the assumption that the noise excursions in the Auger scan were due to Ni. No change in this concentration was found with temperature either for quenched samples or slowly cooled or heated ones.

The structure is identified from the existence of superlattice reflections. The substrate always shows

(2×1) and (1×2) domains, which occur separately on individual terraces at different heights. We determine an average terrace size of $\geq 2000 \text{ \AA}$ on Si(100) by making diffracted-beam profile measurements under conditions at which the waves scattered from terraces at different heights are exactly out of phase. Under these conditions the angular profile of the diffracted beam reflects the average terrace size.⁸ The existence of only one set of seventh-order reflections at each half-order position (see Fig. 1, inset) reveals that the superperiod is normal to the dimerization direction and that (7×2) and (2×7) domains exist on individual (1×2) and (2×1) terraces, respectively. This is not surprising in light of the covalent bonding directions in Si(100).

The degree of order in this superlattice structure can be investigated by analysis of the superlattice beam profile in two orthogonal directions. Figure 1 shows an angular profile collected along path AA' in the inset. The average superlattice period, n , is determined from the position of the superlattice beams. The width of a superlattice reflection in this direction reflects how accurately the superperiod is maintained. We determine that the superperiod is $D \pm \delta = [7 \pm 0.3]a_0$, where $a_0 = 3.84 \text{ \AA}$ is the lattice constant in the unreconstructed surface. The narrow range of values indicates that there are relatively few mistakes [i.e., admixtures of (2×6) and (2×8) units] in the "7" periodicity.⁹ Alternatively one could interpret the width of the superlattice beam along this direction as resulting from finite domains of perfect (2×7) unit meshes with no admixtures of (2×6) or (2×8) . If this were so, however, the intensity of the satellites at

the $2/7$ positions would have to be much greater than is observed.^{9,10}

Analysis of the 7th-order profile along the orthogonal azimuth, path BB' in Fig. 1, gives the average domain size for the (2×7) structure in the "2" direction. A fit to the width of this profile with use of a geometric-size-distribution model¹¹ gives an average domain size $\langle L \rangle \sim 200 \text{ \AA}$, or 25 dimer rows. Thus one can think of the (2×7) structure as consisting of strips of domains on each (2×1) terrace with an average strip width of $\sim 200 \text{ \AA}$. In each of these strips the (2×7) unit mesh boundaries are correlated. From one strip to another the correlation breaks down, most likely through a lateral displacement of the two strips relative to each other in the "7" direction.

In order to determine whether the repeat unit of the superlattice involves more than one layer, it is possible again to take advantage of the fact that ordered regions at different heights will interfere destructively if the diffraction conditions are chosen appropriately.⁸ For a superperiod caused by a bilevel structure, a modulation of superlattice beam intensity occurs with changing momentum transfer, with the intensity highest for the out-of-phase conditions and zero for the in-phase conditions.⁸ If, on the other hand, the superperiod is caused by atoms in one level, superlattice beams appear independent of diffraction condition. Figure 2 shows profiles taken under in-phase and out-of-phase diffraction conditions appropriate for levels separated by 1.36 \AA , the Si(100) interplanar distance. In order to account for possible multiple-scattering effects, measurements were made under several diffraction conditions that all yield the same kinematic diffraction

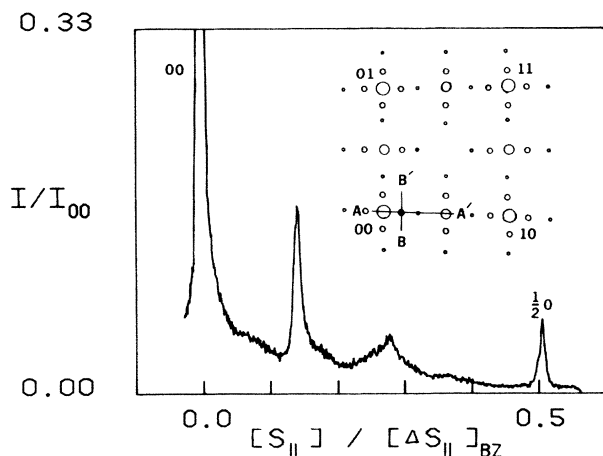


FIG. 1. Angular profile of beams in the (2×7) structure at 500 eV and a grazing angle of incidence of 17.5° . Inset: The diffraction pattern schematically. The solid line AA' in the inset indicates the azimuth in which this profile is taken. The peak intensity of the (00) reflection is ~ 10 times that of the first satellite.

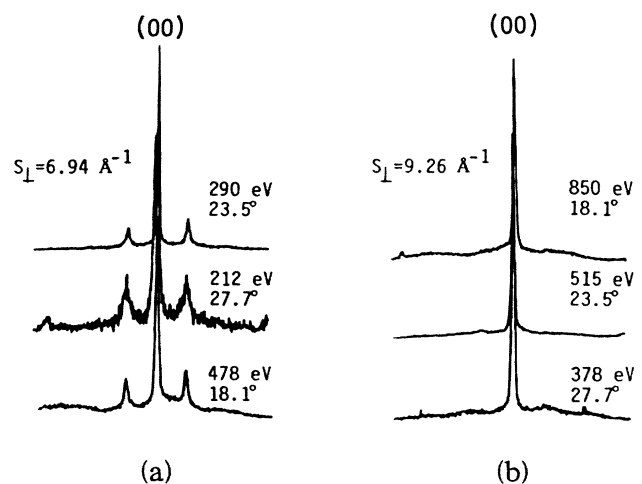


FIG. 2. Angular profiles of the (00) beam and superlattice reflections at two values of the normal component of the momentum transfer, S_\perp . (a) Out-of-phase conditions, (b) in-phase conditions for a layer spacing of 1.36 \AA . All curves are normalized to the same (00) beam intensity.

condition but produce different multiple scattering. Although multiple scattering can cause a complex variation of the intensity ratios of the superlattice and fundamental reflections, it cannot consistently cause or eliminate superlattice reflections in such a way as to mimic a step modulation. We conclude that two levels separated by the Si(100) interplanar distance are involved in the structure. In fact, one can say more. The difference in the integrated intensities in the fundamental reflections under the in-phase and out-of-phase conditions reflects how many atoms are "up" and "down." This can easily be seen by considering a situation where half of the atoms are up and half down. For the in-phase condition, the diffraction does not distinguish up or down. For the out-of-phase condition, there will be complete cancellation of the fundamental reflections, with the intensity appearing in the superlattice reflections.⁸ We have measured profiles under a number of diffraction conditions in addition to those shown in Fig. 2 and averaged the intensities. We observe a ratio of integrated intensities in the 1/7 superlattice reflection and a fundamental reflection of roughly 0.1 for the out-of-phase condition. If one dimer out of seven is missing, the above ratio should be 0.1 [5:1 for each domain, but the intensities from the (7×2) and (2×7) add at the fundamental reflections]. This suggests that on the average one unit is missing in each (2×7) mesh. Some units may, of course, be missing several or none. The fact that not all out-of-phase profiles show precisely the same ratio indicates that multiple scattering is important in a quantitative analysis of these intensities. Removing two dimers produces intensity ratios that lie outside the uncertainties in the above intensity average.

The picture is then the following. Each unit mesh consists preferentially of six "up" units and one "down" unit. This unit mesh repeats almost perfectly, with very little admixture of other mesh sizes. The unit-mesh boundaries are correlated over large distances, creating nearly perfect strips with ~ 200 -Å average width. The only model that appears to fit these criteria is one of ordered dimer defects.¹ One dimer or one atom of the dimer on the average is missing after every six dimers along a row. Figure 3 shows a schematic diagram of the structure. We suggest that the quenching orders dimer defects (vacancies) that exist on the (2×1) surface.

We can furthermore show that (2×*n*) phases created by quenching are metastable and can determine the decay kinetics. We have measured the decay of the integrated intensity of a (2×7) superlattice reflection at several temperatures. The decay is linear on a semilog plot, indicating first-order kinetics, i.e.,

$$d \ln N / dt = -R = -\nu \exp[-\Delta H / kT], \quad (1)$$

where *N* is the number of scatterers in the (2×7)

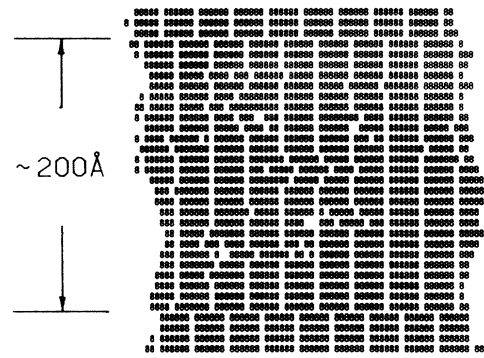


FIG. 3. Schematic diagram of the proposed (2×7) domain structure. Missing-dimer defect sites are correlated over distances of ~ 25 dimer pairs in the "2" direction. In the "7" direction, domain sizes are greater than 500 Å. A unit mesh is indicated by the box in the lower left. It consists on the average of six dimer pairs and one missing dimer pair.

phase and is proportional to the integrated intensity in the superlattice beam, *R* is the rate of the reaction, ν is the preexponential factor, and ΔH is the activation enthalpy of the decay process. First-order kinetics implies that the rate of decay is proportional to the number of entities remaining. A point-defect decay mechanism satisfies first-order kinetics. The nature of this transition (disordering with first-order kinetics) implies one-dimensional disordering. Details will be presented elsewhere.⁹ From the slopes of the decay curves, we have extracted the activation energy and preexponential factor for the decay process. They are $\Delta H = 0.7 \pm 0.2$ eV/atom and $\nu = 6 \times 10^2 \pm 1.5$ sec⁻¹.

We next address under what circumstances these phases form. We have observed the (2×*n*) phases with every Si(100) sample that we have investigated. We have used all the sample preparation techniques that we are aware of including those that produce other superlattice phases on Si(100). In all cases we can quench in the (2×*n*) phase. The only way we have found to eliminate it is by annealing the sample for at least 1–2 h (depending on prior processing) above 1000 °C. With increasing time, the quenched-in superlattice reflections become weaker and move closer to the fundamental reflections (*n* increases), indicating a larger unit mesh and a reduced concentration of point defects that can order. As this occurs, the background in the Brillouin zone away from any reflection also decreases, and the peak-to-background ratio in the (2×1) phase increases. The background continues to decrease after we are no longer able to quench in the phase, indicating that the equilibrium concentration of point defects is still not achieved, i.e., more point defects are required to form the phase than can be supported on the surface at equilibrium. These defects

are apparently very stable, as it is extremely difficult to reduce their concentration.

Once we have eliminated the $(2 \times n)$ phase by extended annealing, we can easily recreate it by sputter etching the surface or oxidizing it. Clearly defects are created in these procedures. We conclude that Si(100) surfaces generally contain an excess of missing-dimer defects that are introduced during (or not eliminated by) surface processing.

Finally, what causes these defects to order? We do not know at present. It could be that at high temperatures an ordered $(2 \times n)$ phase is present that we cannot observe because of thermal diffuse scattering. Without additional conditions on the formation, one would conclude that the phase should then be observable with slow cooling also; it is not. It could be that the formation of the structure is driven by strain energy. Strain could be caused by the redistribution of impurities during quenching; however, we do not observe any impurities at high temperatures and only beam-induced impurities at low temperatures. This does not rule out that a very low concentration of impurities could not produce the effect. An alternative possibility⁹ is that the strain energy is a consequence of the defects themselves. Pandey¹ suggests that dimer defects, although they individually reduce the free energy of the surface, repel each other at close distances because of strain. This strain energy can easily be temperature dependent. An excess concentration of defects at the surface may reduce the total free energy by ordering at high temperatures, but increase the free energy by doing so at low temperatures, where the increased strain energy makes the phase metastable. An ordering in a direction normal to the dimerization direction, as is observed, would appear to create less strain⁹ than an ordering along the dimerization direction. Slow cooling allows the phase to disorder as the sample cools. Rapid cooling freezes in the structure, but at lower temperatures it is metastable and decays with time as the dimer defects randomize again on the surface.

In conclusion, we have shown that Si(100) surfaces

in general contain a greater than equilibrium concentration of missing-dimer defects that are presumably a consequence of surface processing. Their existence is confirmed by the formation of a quenched-in, ordered $(2 \times n)$ phase of missing-dimer defects, which is metastable at temperatures below at least 800°C. The value of n is smaller for larger excess defect concentrations. To what extent these excess defects affect other surface properties is not known, but they clearly affect the total free energy of the surface and could thus easily influence electronic or other structural properties.

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