

Introduction

Since its discovery in 1959 by Schlier and Farnsworth [2] there have been prolific studies on the Si(111) reconstruction. These studies have included, but not been limited to, STM, LEED, UHV-TED, RHEED, REM and, CITS [1-8]. Specifically, STM observations by Binnig et al [1] lead to the proposal of an adatom model of the reconstructed Si(111)-(7x7) surface which was later modified to a dimer adatom stacking-fault (DAS) model [2]. The effects of temperature on the Si(111) surface and the consequentially induced reconstructions as modeled by *ab initio* calculations of the surface between the (1x1) adatom and the (7x7) DAS structures are herein discussed.

The DAS Model

The Si(111)-(7x7) surface was characterized in 1895 by Takayanagi, Tanishiro, Takahashi and, Takahashi as a dimer adatom stacking-faulted (DAS) structure (fig.1)

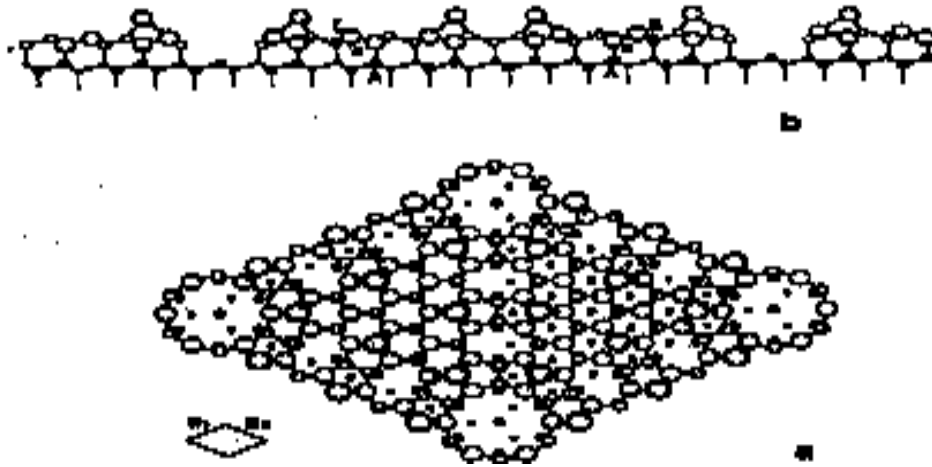


Figure 1. From [2]. Top: side-view Si(111)-(7x7) surface. Heavily outlined large circles represent adatoms, large circles represent stacking-fault layer atoms, small circles represent dimer layer atoms and, dots represent bulk layer atoms. Bottom: top-view of Si(111)-(7x7) reconstructed unit cell.

constituted by 3 main regimes: bulk, reconstruction and, adatom [2]. The bulk regime lies beneath the second reconstruction layer and retains the unreconstructed (111)-(1x1) structure. The second reconstruction layer (fig.2) exhibits a local (1x1) configuration and is formed from 36 atoms of the top-most crystal layer and is the "dimer" in DAS [3].

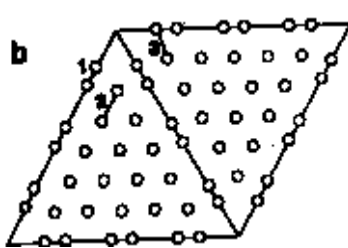


Figure 2. From [2]. Dimer of Si(111)-(7x7) reconstruction.

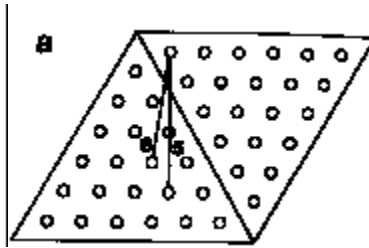


Figure 3. From [2]. Stacking-fault layer of Si(111)-(7x7) reconstruction.

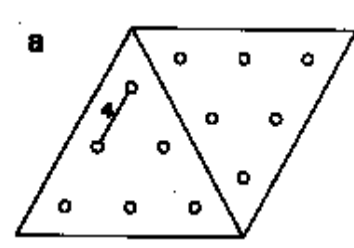


Figure 4. From [2]. Adatom layer of Si(111)-(7x7) reconstruction.

Dimers in the second reconstruction layer are $\sim 8.9\%$ longer than nearest-neighbor (NN) Si-Si bonds at 0.256nm . The first reconstruction layer (fig.3) also exhibits a local (1×1) configuration and constructs the "stacking-fault" for the model's anagram title. The fault from this layer lies on either of the subcells in the (7×7) unit cell. The adatom layer (fig.4) exhibits a local (2×2) configuration and is the product of 12 adatoms in triangular formation. Each adatom is bound to 3 silicon atoms in the stacking-fault layer. This model as posited by Takayanagi et al bodes well with experimental results [2]. The second reconstruction layer fits Patterson peaks (fig.5) 1,2,3 and their symmetric equivalents. The first reconstruction layer fits peaks 5,6,7 and their symmetric equivalents and, the adatom layer fits peak 4 and its symmetric equivalents.

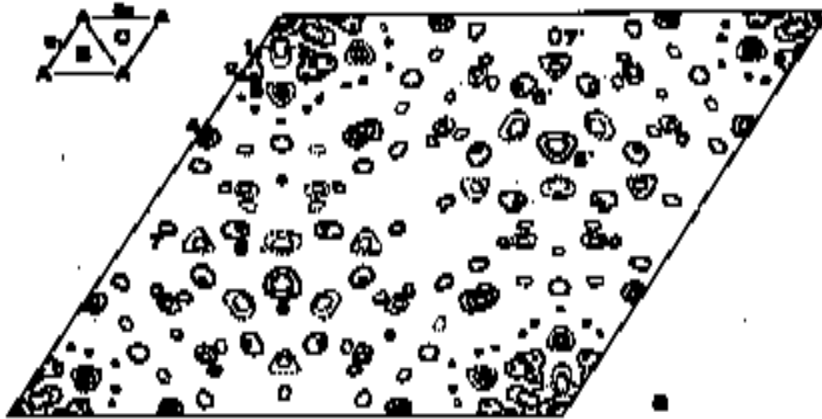


Figure 5. From [2]. Patterson map of Si(111)-(7x7) reconstructed unit cell.

Support for the Model

Scanning Tunneling Microscopy (STM) images obtained by Binnig et al showed the Si(111)-(7x7) unit cell bounded by minima corresponding to empty adatom positions; maxima correspond to the presence of adatoms [3]. Support of the DAS model is evidenced from theoretical and experimental results. Of the models proposed to describe the Si(111)-(7x7) surface, the DAS had the least number of dangling bonds (19) and the lowest energy of all the possible reconstructions for the surface [2,4]. Payne, Roberts and Needs noted that while the (7×7) surface has fewer dangling bonds than the (1×1) surface the two surfaces have the same density of dangling bonds [3,4]. Hamers, Tromp and Demuth attributed the "metallic" nature of the Si(111)-(7x7) at room temperature to its dangling bonds straddling the Fermi level [1]. The surface topography of the DAS model agrees well with Binnig's STM images and, of the models considered, was the most consistent with photoemission, IR and, EELS data [2]. Takayanagi et al also showed the calculated TED intensity distribution (fig.6) of the DAS model to agree well with the TED intensity distribution (fig.7) obtained from the Si(111)-(7x7) surface taken by an incident beam deviated about 0.14 radians from normal. Further, when the adatoms are considered raised and the surface vibrations minimized, the DAS model agrees with RBS data.



Figure 6.From [2]. Calculated TED intensity distribution for DAS model of Si(111)-(7x7) surface.

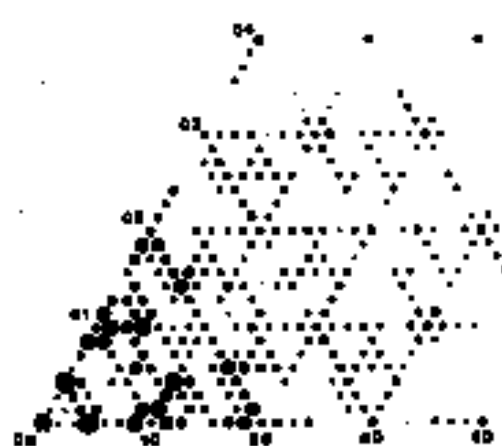


Figure 7.From [2]. TED intensity distribution of Si(111)-(7x7) surface. Incident beam off-normal by about 0.14 radians.

Temperature Effects

In the 1960's Lander noted the (7x7) to (1x1) phase transition of the Si(111) was reversible and occurs at 1100K and, in 1985 Telieps and Bauer pyrometrically determined the transition temperature, T_t , as 1100K (+/- 15K) [5]. LEERM micrographs showed only the (1x1) phase existing when the sample was held at the transition temperature for 1 minute. Nucleation of the (7x7) from the (1x1) was observed when the temperature was lowered to 1094K (fig.8) and within 1 minute most of the Si(111) surface was covered by (7x7) domains (fig.9). When the temperature was returned to 1100K, the transition was observed to reverse (fig.10).

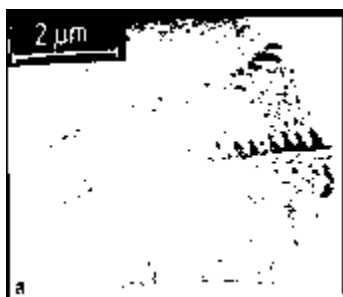


Figure 8.From[5].LEERM micrograph of (1x1) domains with (7x7) domains nucleating (dark triangles).



Figure 9.From[5].LEERM micrograph of Si(111) surface mostly covered by (7x7) domains.



Figure 10.From[5].LEERM micrograph of (7x7) domains returning to (1x1) domains.

Upon lowering the temperature again (this time to 1088K), the (7x7) domains returned, nucleating at steps and terraces. The growth of the (7x7) domains after quenching from temperatures above the transition temperature was observed to retard the transition. The mechanical stress imposed on the surface above the transition temperature is considered to aid the (7x7) reconstruction upon cooling. Telieps and Bauer concluded the transition between the (7x7) and (1x1) surface structures to be first-order because the structures in all the LEERM micrographs appeared to be clearly separated.

Modeling the Model

Total Surface Energy Calculations

In 1989 Payne et al used total energy pseudopotential calculations of the Si(111) sub-structure to determine the mechanism responsible for the stability of Takayanagi reconstruction [3]. They concluded that transition is of the first-order and that the presence of a stacking fault is indicated by the first layer of atoms forming triangular islands in each of the reconstructed (7x7) sub-cells. Islands on one half of the Si(111)-(7x7) are rotated by 180° from islands on the other half. The low energy of the reconstructed surface is considered to be the product of a favorable energy of interaction between the elements of the structure. That is, if the energy of combined elements is less than the sum of the individual energies, then the interaction between those elements is energetically favorable. Payne et al used calculations of the total energies of reconstruction on the germanium (111) surface to show that the Takayanagi structure in the absence of adatoms was not low in energy but, the addition of adatoms, thereby completing the structure, showed a reduced surface energy (table 1).

	Energy per $n \times n$ unit cell (eV)	Energy per surface atom (eV)
1x1 unrelaxed	1.22	1.22
1x1 relaxed	1.15	1.15
2x2 adatom over second layer atom	4.16	1.04
2x2 adatom over fourth layer atom	4.5	1.13
3x3 Takayanagi without adatoms	10.06	1.12
3x3 Takayanagi	7.95	0.88

Table 1. From [3]. Total energies of Ge(111) surface reconstructions.

It was also found that the Takayanagi structure with adatoms had reduced dimer bond lengths of 0.256nm from the non-adatom structure's 0.260nm. This reduced dimer bond length towards the bulk bond length consequently reduced the strain energy on those dimer bonds, thus yielding a surface energy reduction greater than expected and further serving to stabilize the DAS structure.

Calculating Diffuse Scattering Patterns

Sakamoto and Kanamori in 1991 used Monte Carlo (MC) simulations based on a lattice gas model to describe the high temperature phase of the Si(111)-(1x1) surface [6]. By letting two particles be distinguished relative to adatoms on a normal or stacking faulted substratum and representing those particles as equilateral triangles with vertices corresponding to substratum atoms bonding with adatoms, they were able to describe the existence of two orientations for the triangles with respect to normal or stacking faulted substratum. The available sites for the particles were assumed to make a triangular net; such that, the interactions between triangles of different orientations at second neighbor sites were assumed to have three-fold symmetry. Interactions between triangles of the same orientation at second neighbor sites was assumed to have six-fold symmetry. The energy of the Si(111) model was obtained by modifying that for the germanium (111) surface

$$E_{Ge} = \sum_i V_i p_i \quad (i = 0, 1, \dots, 6) \quad (1)$$

$$E_{Si} = V_2 p_2 + V'_2 p'_2 + V''_2 p''_2 + V_3 p_3 + V'_3 p'_3 \quad (2)$$

where, p_i and p'_i are the number of i th neighboring pairs of similar and differing triangles, respectively and; V_i and V'_i are the interaction energies of those neighboring pairs. Two kinds of second neighboring pairs with different orientations are distinguished by p'_i and p''_i and, their respective interaction energies are V'_i and V''_i . The interaction energy V_1 for Si(111) is assumed infinite and thus omitted in equation 2. The value $V''_2 p''_2$ is assumed to be zero, V_2 is assumed to be a positive number and, the concentration of particles is assumed to be slightly less than 12/49. Calculated diffuse scatterings involving the above caveats showed spots around the (3 x 3) Bragg points at temperatures immediately above the transition temperature. This was in good accordance with experimental observations of Ino in 1977 and Iwasaki et al in 1987 [6].

Calculating the Reconstructive Phase Transition

A quasi-2D four-state planar model yielding a calculated first-order transition for the Si(111)-(7x7) reconstruction was posited in 1996 by Itoh [7]. For the model of the DAS structure, atoms in the lower half of the middle layer or top most bilayer are considered as discrete planar rotors and, their interactions are restricted to NN. By focusing on the atomic configurations of the dimer layer, it was possible to consider only the in-plane motion of the atoms as 3-point discrete rotors (3PDR's) on a 2D triangular lattice. The rotors were next restricted to four distinct states (US, FS, DA and, DB); where, US and FS states represented unfaulted and faulted stacking atoms, respectively. DA and DB represented dimer atoms (fig.11).



Figure 11. From [7]. Defined atomic states of 3PDR model. DA and DB represent dimer atom states. US and FS represent stacking atom states.

By compensating for the absence of a dimer contraction term with an energy benefit, a five-part Hamiltonian was constructed

$$H = H_0 + H_1 + H_2 + H_3 + H_4 \quad (3)$$

$$H_0 = -J_0 \sum_{x,x'} \{ s(x), (x') \quad (x), - \quad (x), US \quad (x'), FS \} \quad (4)$$

$$H_1 = -J_1 \sum_x \left[\begin{aligned} & z_3 \quad (x), DA \quad (x+a_i), DB \\ & \times \left[\begin{aligned} & (x-a(i+1)), US \quad (x-a(i+2)), FS \\ & + (1- \quad (x-a(i+2)), FS) \quad (x-a(i+1)), US \end{aligned} \right] \end{aligned} \right]$$

$$+ (1 - \delta_{(x-a(i+1)),US} \delta_{(x-a(i+2)),FS}) \quad (5)$$

$$H_2 = -J_2 \sum_x \sum_{z3} \delta_{(x),DB} \delta_{(x+ai),DA} \times [\delta_{(x-a(i+1)),US} \delta_{(x-a(i+2)),FS} + (1 - \delta_{(x-a(i+2)),FS} \delta_{(x-a(i+1)),US}) + (1 - \delta_{(x-a(i+1)),US} \delta_{(x-a(i+2)),FS})] \quad (6)$$

$$H_3 = -J_3 \sum_x \sum_{z3} \delta_{(x),DA} \delta_{(x+ai),DB} \times \delta_{(x-a(i+1)),US} \delta_{(x-a(i+2)),FS} \quad (7)$$

$$H_4 = - \sum_x (\delta_{(x),US} - \delta_{(x),FS}) \quad (8)$$

where, $\delta_{(x),US}$ and $\delta_{(x),FS}$ are the Kronecker delta functions and the J_i coupling constants are positive and satisfy the inequalities

$$J_1/J_0 > J_2/J_0 > J_3/J_0, \quad J_4/J_0 > 0 \quad (9)$$

the summations to \sum_x are taken over all NN pairs x and x' on the triangular 2D lattice, $\delta_{(x),US}$ is defined as the collective notation for the US and FS states, $\delta_{(x),DA}$ describes a 3PDR state at site x on $\delta_{(x),DB}$ which has adopted one of the four states and, $\delta_{(x),DB}$ is a Kronecker delta

$$\text{Re: } \delta_{(x),DB} = \delta_{(x),DB} \quad (10)$$

The particular combination of these Hamiltonian operators serves to ensure thermodynamic stability from low to high temperatures as well as from the combinations and positions of the silicon atoms. H_0 derives the locally ordered US and FS structures where adatom and rest-layer atoms are assumed to lie above the plane of the 3PDR's for adequate correlation to the real reconstructed surface. This operator also ensures low temperature order by reducing the model to a 2D Ferromagnetic Ising model. The second and third terms essentially describe the 3-point and 4-point dimer adatom interactions (DAI) in figures 12 and 13.



Figure 12. From [7]. 4-point and 3-point interactions described by H_1 .



Figure 13. From [7]. 4-point and 3-point interactions described by H_2 .

The combination of H_1 and H_2 serves to connect pairs of DAI such that straight dimer rows are formed. It can be seen that the 3-point interactions described by H_1 and H_2 may effectively constitute their respective 4-point interactions; such that, by rewriting the equations to the form

$$H_1 = -J_1 \sum_x \sum_{z3} \delta_{(x),DA} \delta_{(x+ai),DB} \times [(-2) \delta_{(x-a(i+1)),US} \delta_{(x-a(i+2)),FS}]$$

$$+ \quad (x-a(i+1)),US + \quad (x-a(i+2)),FS] \quad (11)$$

$$H_2 = -J_2 \sum_x \sum_z \sum_{(x),DB} \sum_{(x+ai),DA} \times [(-2) \quad (x-a(i+1)),US \quad (x-a(i+2)),FS + \quad (x-a(i+1)),US + \quad (x-a(i+2)),FS] \quad (12)$$

and by letting $\beta = 2$, the 4-point interactions are decoupled. The mere presence of the H_3 operator is enough to secure stability of the corner holes at the edges of the Si(111)-(7x7) surface. Finally, the last term has the general form of a static external magnetic field and serves to secure the stability of figures 14 and 15.



Figure 14. From [7]. Orientation of atoms in US domain.

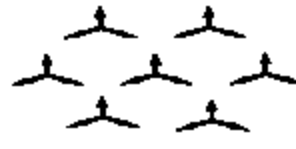


Figure 15. From [7]. Orientation of atoms in FS domain.

The H_4 operator is also necessary study of the high temperature phase of the model. Figure 16 shows the calculated (7x7) reconstructed surface during the annealing process.

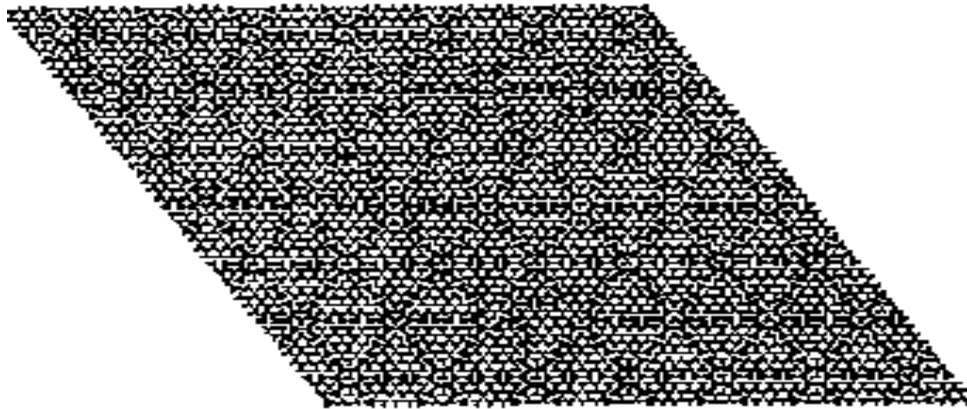


Figure 16. From [7]. Calculated Si(111)-(7x7) reconstructed surface after annealing.

Conclusion

Several mathematical models of the reconstructed Si(111) surface and its temperature induced transition between the (1x1) and (7x7) structures have been devised. While the approaches taken for the individual models have differed, each serves to justify the stability of the reconstructed (7x7) DAS surface as described by Takayanagi et al [1] and each indicates that the transition is typical of a first-order phase transition [6,7,8]. In particular, *ab initio* calculations performed by Itoh confirmed that DAI interactions play prominent roles in the stability of the arrangement of atoms in the DAS model and the reconstructed surface as a whole [7]. Further, of the four states to which the atoms were confined their calculations showed the FS domains as an embryonic phase at high temperatures. An earlier study by Kohmoto and Ichimiya [8] supports the calculated first-order phase transition and reconstruction's dependence on the DAI. Rocking curves

of RHEED intensities from the Si(111) surface showed the transition from the DAS (7x7) to the adatom (1x1) structure to occur via dissolution of the stacking-fault and breaking of the dimer bonds.

References:

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Temperature Induced Si(111) Reconstruction as Represented by the DAS
Model and Supporting *Ab Initio* Calculations of the Model

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