

Determination and Refinement of the Ag/Si(111)-(3 × 1) Surface Structure

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A new model for the Ag/Si(111)-(3 × 1) surface is proposed based on direct phasing of transmission electron diffraction data. The atomic positions in the model are refined using dynamical diffraction calculations. Other existing models were simulated and could not fit the diffraction pattern. The new model is consistent with the experimental results reported in the literature on this surface. [S0031-9007(98)05353-8]

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Much research has focused on submonolayer coverages of alkali metals on the Si(111) surface due to their unique effects on Si oxidation. When deposited at room temperature, the alkali metals promote oxidation and could be useful in a low temperature microchip processing step to form gate oxides without losing sharp doping profiles [1]. When deposited at elevated temperatures, they form a (3 × 1) surface structure which inhibits oxidation [2]. The mechanisms giving rise to such widely differing behaviors are not completely understood, in part due to the fact that the (3 × 1) structure is unknown. Low-energy electron diffraction (LEED) *I-V* curves suggest that the same Si(111)-(3 × 1) structure is induced by Li, Na, Mg, and Ag independent of adsorbate type [3,4]. While the adsorbate coverage was initially debated, careful measurements based on ion scattering spectroscopy [5] and on Auger electron spectroscopy combined with scanning tunneling microscopy (STM) [6] have shown that the saturation coverage is one adsorbate atom per 3 × 1 unit cell. Similarities between STM images of Li/(3 × 1) and Ag/(3 × 1) [7] along with the similar Si 2*p* core level spectra obtained from Na/(3 × 1) [8,9], Mg/(3 × 1) [10], and Li/(3 × 1) [11] have reinforced the idea that one structure, predominately made up of Si atoms, is formed by many different elements on the Si(111) surface.

Several groups have noted that the (3 × 1) surface electronic properties resemble those of the native Si(111)-(2 × 1) structure. Figure 1 shows the (2 × 1) structure [12] along with three related models proposed by Okuda *et al.* for the (3 × 1) surface [8]. The model shown in Fig. 1(b) was independently proposed by Erwin [13] who has referred to it as an extended Pandey chain [14]. The structure in Fig. 1(c) can be described as a Seiwatz chain [15] with a neighboring row of adsorbate atoms sitting in *T*₄ sites. Sakamoto *et al.* [16], Weitering *et al.* [17], and Wong *et al.* [18] each proposed a variant of the Seiwatz model with the adsorbate atoms moved to *T*₁ sites halfway in between the silicon chains. The model in Fig. 1(d) has received relatively little attention since being proposed. Even though total energy calculations have shown that either the extended Pandey [13] or the Seiwatz [19] structure has the lowest surface energy for

the currently proposed models, neither structure can fully account for experimental angle-resolved photoemission data [11,20].

Using transmission electron diffraction, we find a new model [Fig. 2(a)] for the Ag/Si(111)-(3 × 1) surface. A partial silicon double layer with a silicon chain has a missing row where the adsorbate atoms lie. The Ag atoms bond to a single atom in the silicon chain on one side of the trench and can bond to one of two atoms in the partial double layer on the other side. In this way, by choosing either the partial double layer atom in the $[\bar{1}10]$ direction or the one in the opposite direction, the Ag atom breaks the mirror symmetry along $[11\bar{2}]$. Both possible Ag sites are shown in Fig. 2(a). All of the Ag atoms in a single row would have to shift in the same direction to accommodate all of the dangling bonds, but one can postulate the

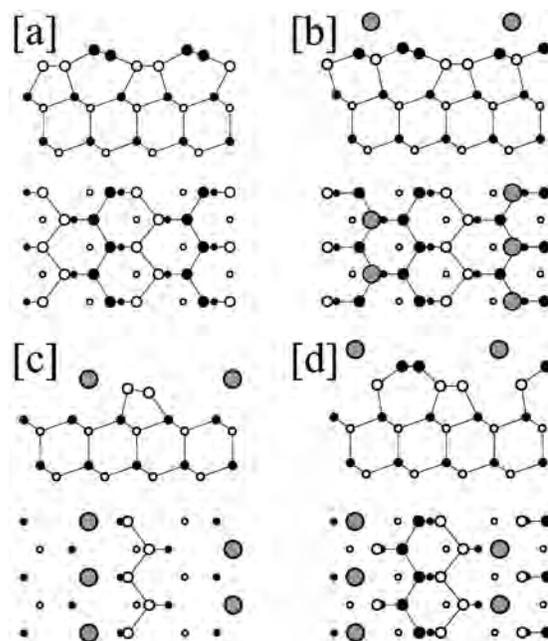


FIG. 1. (a) The native Si(111)-(2 × 1) surface reconstruction with similar models proposed for the adsorbate-induced Si(111)-(3 × 1) reconstruction: (b) extended Pandey chain, (c) Seiwatz chain, and (d) a modified missing-row structure. The grey circles represent adsorbate atoms.

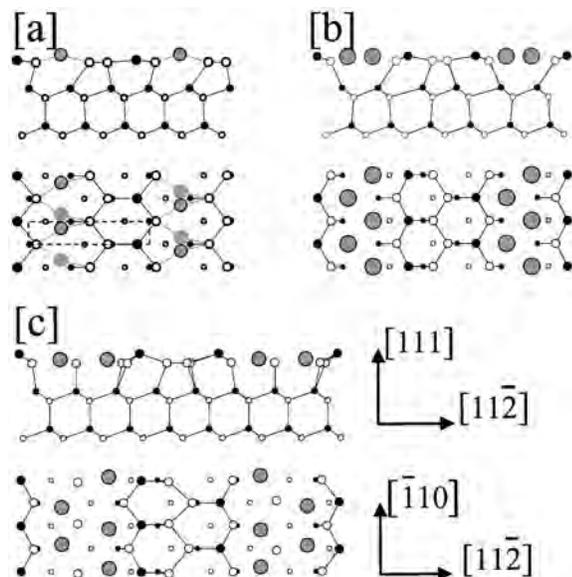


FIG. 2. (a) Proposed model of Ag/Si(111)-(3 × 1) surface along with related structures of (b) In/Si(111)-(4 × 1) and (c) Au/Si(111)-(5 × 2). One cm asymmetric unit is outlined in (a) with the bottom left corner of the unit corresponding with the origin for atomic positions listed in Table I. The grey circles represent metal adsorbate atoms with the two shades of grey in (a) separating two equivalent Ag sites (see text). For the (5 × 2) structure, the registry of the top layer of atoms with the bulk was not determined in Ref. [25] and is inferred; a partially occupied Si adsorption site has also been left out to highlight the similarities with the other structures.

propagation of a surface dislocation traveling the length of a trench, thereby shifting every Ag atom in that row. Such a picture explains the deviation from cm symmetry towards $p1$ symmetry seen in STM images [7,21,22] as well as the tip-induced shifting of entire rows between scans [22]. The model in Fig. 2(a) can also account for data linking the Ag/Si(111)-(3 × 1) and the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) structures. The fact that the ($\sqrt{3} \times \sqrt{3}$) structure can be formed at room temperature by deposition of Ag on a preexisting (3 × 1) surface reveals a low activation energy barrier [23]. This, coupled with the observation of similar Ag MNN Auger line shapes for (3 × 1) and ($\sqrt{3} \times \sqrt{3}$) [6], points to a similar local bonding geometry for Ag in both structures. Each Ag atom in Fig. 2(a) bonds most strongly to a single Si atom in the Si chain and has two other Si atoms surrounding it. Similarly, in ($\sqrt{3} \times \sqrt{3}$), an Ag atom bonds most strongly to a single Si atom in a Si trimer and has two other Si neighbors on the surface. Finally, the new (3 × 1) structure model is compelling because of its closeness to other $n \times 1$ or $n \times 2$ structures formed by metal adsorbates on the Si(111) surface. Shown in Figs. 2(b) and 2(c) are recently solved structures for the In/Si(111)-(4 × 1) [24] and the Au/Si(111)-(5 × 2) [25] surfaces. All three surfaces can be described in the same general terms. A partial silicon double layer containing a Si chain and either one or two missing rows leaves a trench parallel to $[\bar{1}10]$ in which the adsorbate atoms lie.

The data for this study were obtained in an UHV Hitachi H9000 TEM attached to surface analysis and film deposition systems [26]. The sample was a 3 mm Si disk that was dimpled, polished, and then chemically etched to electron transparency. Cycles of ion milling (1 kV Ar⁺) and annealing at 750 °C were used to clean the surface until a sharp Si(111)-(7 × 7) diffraction pattern was seen in the microscope. After room temperature deposition of Ag and an anneal at 550 °C for several seconds, both the (3 × 1) and the ($\sqrt{3} \times \sqrt{3}$) diffraction patterns could be detected. Diffraction intensities were recorded on a series of nine films with varying exposure times from 0.5 to 120 s, covering the wide dynamic range in the diffraction pattern. The sample was tilted slightly away from the (111) zone to weaken the bulk diffraction beams relative to the surface beams. The intensities on the nine films were digitized, measured, and then averaged [27] to produce a final data set with estimated measurement errors. Two separate data sets were collected and reduced in this way to give a total of 90 different (3 × 1) surface beam measurements. Of the 90 measured intensities, 56 had errors between 4% and 30%, 26 had errors between 30% and 55%, and 8 had errors between 55% and 90%.

One of the difficulties in studying unknown surface structures through diffraction techniques has been the lack of a starting point from which to refine atomic positions. An initial guess must be made which has to be close to the correct structure if the global minimum is to be found. In a case like the Ag/Si(111)-(3 × 1) structure, where the STM images are strongly bias dependent and not easily interpretable [22], diffraction techniques would normally be limited to testing out currently proposed models. However, with the recent progress made in applying direct phasing methods to surface diffraction data [28], surface diffraction is becoming an *ab initio* technique. Direct methods were applied to the electron diffraction data in this study as a first analysis step, and they provided the key to finding the solution of the Ag/(3 × 1) structure.

The technique of direct phasing approaches the diffraction phase problem by exploiting known probability relationships which exist between the intensities and the phases of diffracted beams. Essentially, a numerical procedure is set up which finds sets of phases for a given set of intensities which best satisfy these probability relationships. The only pieces of information fed into the direct phasing analysis are the measured intensities and an assumption about the solution's symmetry. STM images of the (3 × 1) structure belong to the $p1$ plane group, although the deviations from cm symmetry appear to be minor. For completeness, we analyzed the data in both $p1$ and cm plane groups. By taking the most probable sets of phases found in the phasing analysis and combining them with the measured intensities, the diffraction pattern can be Fourier transformed back into a scattering potential.

The solutions found by the direct phasing analysis all showed slight variations of one basic scattering potential (Fig. 3). Four well-resolved peaks labeled A, B, C, and

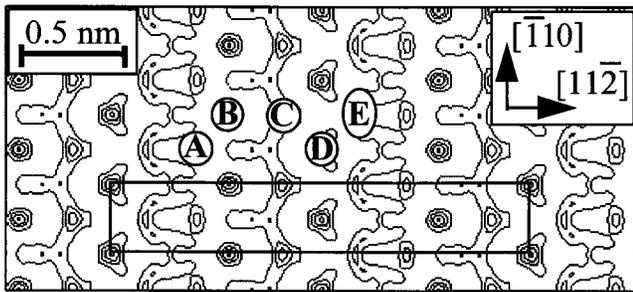


FIG. 3. Contour map of scattering potential found through direct phasing. Peaks A, B, C, and D correspond to Si atoms, and peak E corresponds to two half-occupancy Ag sites. A centered 6×1 unit cell is drawn showing the cm symmetry.

D can be seen along with one elongated area labeled E. The four well-resolved peak positions were taken as initial atom sites from which to start simulating the measured diffraction intensities. The elongated region was considered to represent either two partially occupied atom sites or an artifact arising from the lack of a complete data set in reciprocal space. As an initial diffraction intensity fitting step, both interpretations for the elongated area were tried along with the permutations of placing one Ag atom at one of the sites and Si atoms at the remaining sites. Only one layer of atoms was modeled kinematically, and the effects of the bulk crystal and dynamical diffraction were neglected. The best fit found under these conditions gave a reduced χ^2 value of 4.49 for the case of Si atoms at positions A, B, C, and D and two half-occupied Ag sites at position E corresponding to the top double layer in our proposed model. The next best fit for another permutation of Ag and Si atoms among the A–E sites was much worse with $\chi^2 = 8.46$.

For the final fitting procedure, the bulk crystal and dynamical effects were accurately modeled. As mentioned earlier, the sample was tilted off of the (111) zone to weaken the bulk diffraction. Both this angle of crystal tilt and the thickness of the sample were found by measuring the bulk diffraction intensities and fitting them with the sample thickness and tilt as the only two variables in a multislice calculation. The best fit values for the thickness of the two sample areas (45 and 48 nm) agreed with the thickness estimated from parallel electron energy loss spectroscopy (PEELS) data [29] within the PEELS measurement error. With the values for the bulk parameters, we added two reconstructed double layers to the surface and again used multislice calculations to find the (3×1) surface beam intensities. Allowing one bulk double layer to relax with our proposed model for the surface atoms gave $\chi^2 = 2.81$. The fit included 14 parameters: 12 for atom sites and a Debye-Waller factor for both the Ag and the surface Si. The Ag occupancy was set at 0.5 for the two equivalent Ag positions to model a disordered arrangement of the $[\bar{1}10]$ shifts on the surface. We note that the disorder is not inconsistent with the STM images. While Ag atoms in a single row parallel to $[\bar{1}10]$ are well

ordered and predominately shift in the same direction, the correlation between neighboring Ag rows is weak and the disorder along the $[11\bar{2}]$ direction is high.

For comparison, we modeled the other currently proposed structures for the (3×1) surface. Several variations on each model were explored including different registries between the substrate and the surface atoms and possible displacements of Si surface atoms in the $[\bar{1}10]$ direction. One relaxed double layer and two or three Debye-Waller factors were always included, keeping the number of fitting parameters between 12 and 16. The best fit obtained with an extended Pandey chain model was $\chi^2 = 7.54$. Seiwatz models were tried with Ag at T_1 and T_4 sites resulting in a best χ^2 of 6.35. The type of model shown in Fig. 1(d) yielded a $\chi^2 = 4.33$.

Allowing two bulk double layers to relax with our proposed model lowers the χ^2 value to 1.62. The 18 atomic sites varied in this fit are shown in Table I along with three Debye-Waller factors and a refined occupancy for the Ag sites. Estimated errors were calculated within a 68% confidence limit, taking into account correlations between all variables. For the relaxed subsurface layers, in which the atoms are only slightly displaced from their bulk positions, we found that the relative atomic positions within the layer were determined more precisely than the position of the layer as a whole with respect to the bulk crystal. This is a consequence of the fact that the data set includes no bulk reflections and consists entirely of surface superstructure intensities. Accordingly, two errors are listed for each layer in Table I. The first, σ (layer), represents the 68% confidence limit with respect to shifting the entire layer as a whole relative to the bulk. The second, $\langle\sigma_{\text{rel}}\rangle$, is an average value for the uncertainties in the relative atomic positions within the layer. Individual values of σ_{rel} for pairs of atoms were all found to lie within 50% of $\langle\sigma_{\text{rel}}\rangle$ for a given layer. The possibility of Si atoms shifting in the $[\bar{1}10]$ direction was also explored; however, displacements of Si atoms along $[\bar{1}10]$ were not significant and did not improve the fit. The value 0.43 ± 0.04 for the Ag occupancy suggests a slightly lower coverage than $\frac{1}{3}$ of a monolayer and is consistent with previous estimations of the adsorbate coverage on (3×1) surfaces. Weitering *et al.* [17] have suggested that different surface preparation conditions may lead to different levels of adsorbate vacancy defects, thus explaining the range of coverages reported in the literature. While our observation is consistent with this view, it is not conclusive as the error on the occupancy increases to ± 0.12 at the 99% confidence limit. It is interesting to note possible differences between the Ag-induced (3×1) structure and alkali-induced (3×1) . Surface x-ray data from Li/ (3×1) and Na/ (3×1) have been fit by a similar model [31] to the one proposed here for Ag/ (3×1) . The x-ray model for the alkali metals is more symmetric than our Ag/ (3×1) with no deviations from cm symmetry. This agrees well with STM images which show cm symmetric images for the alkali (3×1) surfaces [5,7] and $p1$ symmetric images for Ag/ (3×1)

TABLE I. Ag/Si(111)-(3 × 1) atomic positions in terms of $c(6 \times 1)$ unit cell in cm plane group: $a = 19.953 \text{ \AA}$, $b = 3.840 \text{ \AA}$. All y positions were fixed except for the Ag site, $\sigma_y = \pm 0.0029$. Ag occupancy was fit with 0.43 ± 0.04 , and isotropic Debye-Waller factors (defined as $B = 8\pi^2\langle u^2 \rangle$, where $\langle u^2 \rangle$ is the mean square atomic displacement) were fit at $6.32 \pm 1.5 \text{ \AA}^2$ for Ag, $3.20 \pm 0.46 \text{ \AA}^2$ for surface Si, and $0.47 \pm 0.22 \text{ \AA}^2$ for layers 1 and 2 Si. (In pure bulk samples at 280 K, $B = 0.70 \text{ \AA}^2$ for Ag and $B = 0.46 \text{ \AA}^2$ for Si [30]). For the errors σ (layer) and $\langle \sigma_{\text{rel}} \rangle$, see text.

Atom	x	x (unrelaxed)	y	z (inferred)	σ (layer)	$\langle \sigma_{\text{rel}} \rangle$
Ag	0.132	...	0.350	Surface	0.0015	0.0015
Si	0.449	...	0.000	Layer		
Si	0.028	...	0.000			
Si	0.327	...	0.000			
Si	0.252	...	0.500			
Si	0.000	0.000	0.500	Layer 1	0.0020	0.0012
	0.172	0.167	0.000			
	0.344	0.333	0.500			
Si	0.068	0.056	0.500	Layer 2	0.0040	0.0014
	0.229	0.222	0.000			
	0.397	0.389	0.500			
Si	0.068	0.056	0.500	Layer 3	0.0084	0.0014
	0.235	0.222	0.000			
	0.401	0.389	0.500			
Si	0.139	0.111	0.000	Layer 4	0.0023	0.0009
	0.309	0.278	0.500			
	0.470	0.444	0.000			

[7,21,22]. The difference may be due to atomic size and number of valence electrons. Ag may readily form two bonds long enough to bridge the trench parallel to $[\bar{1}10]$, thus breaking the cm symmetry, while the monovalent alkali metals might only form one bond on one side of the trench and thereby preserve the mirror along the $[11\bar{2}]$ direction.

In summary, by applying direct methods to surface diffraction data, we have found a new model for the Si(111)-(3 × 1)/Ag surface which can explain a large body of experimental evidence. Consisting mostly of Si atoms, the model accounts for the insensitivity of LEED, photoemission, and STM to the specific adsorbate type. The displacement of the Ag atoms along $[\bar{1}10]$ explains the shifts seen in STM images. The Auger data and room-temperature deposition experiments suggesting a link between the $(\sqrt{3} \times \sqrt{3})$ and the (3×1) structures can be accounted for by noting the similar local bonding geometries between the new (3×1) model and the accepted $(\sqrt{3} \times \sqrt{3})$ model. Also, similarities with the native (2×1) structure are in qualitative agreement with the (3×1) surface electronic data. Whether the proposed structure can quantitatively account for the surface electronic data represents a critical test for the new model.

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