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Refined structure of $(\sqrt{3}\times\sqrt{3})$ Sb/Si(111)

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Abstract

Refined structure of $(\sqrt{3}\times\sqrt{3})$ surface reconstruction induced by Sb adsorbed on Si(111) was obtained from X-ray diffraction, using a Patterson function and a least-squares fit. A wide range of reciprocal space was probed to get information for the lateral and the vertical displacements of adsorbate and the top layers of Si. The Patterson function confirms the "milk stool" trimer model, which, according to a least-squares fit, is centered on the T_4 site. The thermal vibration amplitudes of Sb ad-atoms and those of surface layers of Si were obtained and comparison with the values in other surfaces are made. © 1997 Elsevier Science B.V.

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1. Introduction

The surface reconstruction resulting from the adsorption of foreign atoms has been one of the most extensively studied subjects in surface science because of the alteration of electronic properties of the surface by adsorption, which attracts significant interest from fundamental and technological points of view [1]. In particular, the surface reconstruction of Si induced by Sb draws interest due to the technological importance in the fabrication of Sb doped Si devices [2–4].

It has been reported that a clean Si(111) surface tends to form a $(\sqrt{3}\times\sqrt{3})$ reconstruction by adsorption of group III metals (Al, Ga, In) [5–7]. In contrast, the occurrence of a simple (1 × 1) structure by a column V metal, As, was reported [8]. Unlike As, a $(\sqrt{3}\times\sqrt{3})$ reconstruction of Sb on Si(111) was observed from a low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) study [9]. Since then many groups have studied the structure and a couple of structural models were proposed. Abukawa et al. proposed a trimer model of "milk stool" structure obtained from X-ray photoelectron diffraction study [10] and the same result was obtained using scanning tunneling microscopy [11]. Woicik et al., using back-reflection X-ray standing waves and surface extended X-ray absorption fine structure, support the milk stool model, too [12]. More recently, X-ray diffraction data was obtained in favor of Abukawa et al.'s model [13]. Nakatani et al. had difficulty in determining the structure of the system thoroughly from the data presented because the information concerning the lateral adsorption site was insufficient. However, with further work they were able

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to support a T_4 model over a H_3 model, but no detailed analysis was given with it [14].

2. Experimental

In this work we investigated the detailed structures of a trimer and Si substrate below it using in situ X-ray diffraction. A wide range of reciprocal space was probed to obtain information regarding lateral and vertical displacements of each atom. A trimer model was confirmed by the Patterson function and the structural properties of Sb and Si are presented.

X-ray measurements were done with the five-circle diffractometer combined with the molecular beam epitaxy (MBE) chamber [15] on beamline X16A of National Synchrotron Light Source at Brookhaven National Laboratory. Two Si(111) monochromator crystals were used to select 1.12 Å wavelength X-rays. The sample was mounted inside the MBE chamber with the center of its face at the intersection of the diffractometer axes. A position sensitive detector was used with a 2 mm × 10 mm slit, but no analyzer was used. The hexagonal unit cell was chosen so that $a=b=3.839$, and a and b were parallel with $[0\bar{1}1]$ and $[\bar{1}10]$, respectively. This coordinate system was used for indexing the X-ray diffraction data.

In the MBE chamber, a clean Si(111) (7×7) reconstruction was prepared by flashing the Si sample prior to Sb deposition. The (7×7) reconstruction was confirmed by measuring the 1/7th order in-plane peak. Sb was evaporated from a Knudsen cell and the 1/7th order in-plane peak disappeared as Sb was adsorbed on the clean Si(111) surface. The appearance of a 1/3rd order in-plane peak assured that the $(\sqrt{3}\times\sqrt{3})$ structure was rendered. While watching the intensity of the 1/3rd order peak (1/3, 1/3, 0.2) the preparation conditions, that is, dose rate and sample temperature, were optimized for maximum intensity. Because Sb layers dissociate from the surface around 600°C, an abrupt drop of the signal was observed as soon as the dose was stopped at a sample temperature of around 600°C. To maintain the signal, it was found better to maintain dosing during cooling of the sample from ~600 to ~400°C and cease dosing below ~400°C. The reconstructed surface stayed uncontaminated over the time scale of measurement with our base pressure $<2\times10^{-10}$ Torr. For each data point, a scan of diffractometer angle θ was done such that the integrated intensity could be obtained by subtracting the background intensity [16]. Data were collected along the surface normal direction for three fractional-order and three integer-order rods. Fractional-order in-plane peaks were measured to calculate the Patterson function. For reliability of data, measurements were repeated for the symmetry equivalent positions and the integrated intensity was averaged over each symmetry equivalent data point.

3. Results and discussion

Shown in Fig. 1 is a Patterson function [17,18] obtained from the fractional-order in-plane peaks data set resulting from the $(\sqrt{3}\times\sqrt{3})$ surface reconstruction. The six peaks in the Patterson function are predominantly Sb–Sb inter-atomic vectors in the surface reconstruction, consistent with a simple triangular arrangement of heavy Sb atoms, such as exists in the "milk stool" trimer model [10]. This is one of the clearest evidences of a trimer obtained from X-ray diffraction data. Therefore, we started our fitting model with one trimer of Sb atoms in the $(\sqrt{3}\times\sqrt{3})$ unit cell (Fig. 2). The numbered peaks in the Patterson function are associated with the inter-atomic vectors labeled in Fig. 2. The location of the center of the trimer is not determined from the Patterson, and both T_4 and H_3 sites are possible while maintaining the full surface symmetry. Our fit was in favor of a T_4 site with $\chi^2=3$ compared with $\chi^2=12$ in the case of a H_3 site, which is in agreement with the result obtained in Ref. [13].

In Ref. [11] Mårtensson et al. calculated the displacements of Sb and surface layers of Si atoms of the fully relaxed trimer structure through minimization of the Hellmann–Feynman forces at $T=0$. Their results are listed in Table 1. In their calculation, they obtained the same displacements

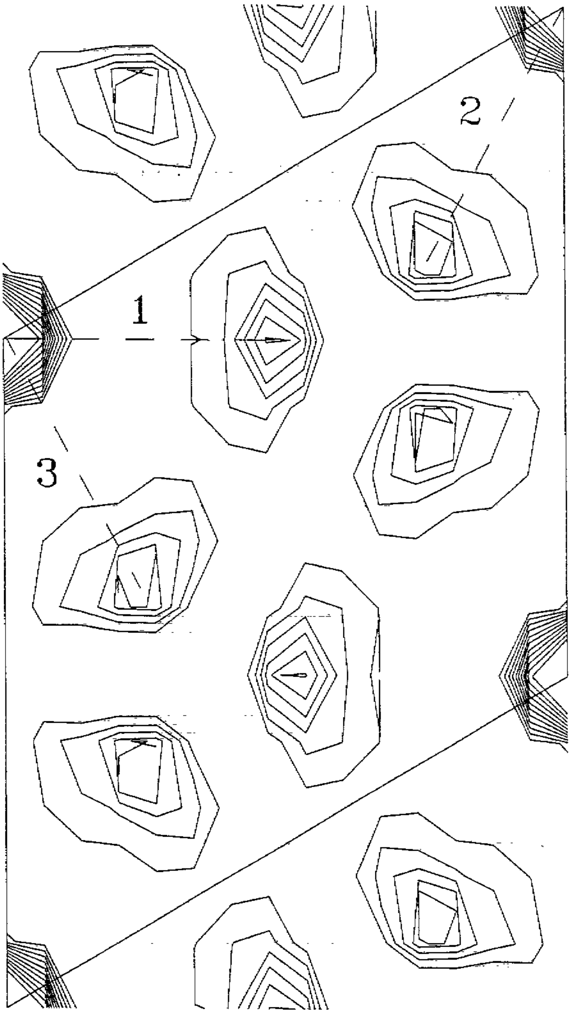

Fig. 1. Patterson function of Sb $(\sqrt{3}\times\sqrt{3})$ structure on Si(111). Peaks are identified with numbers corresponding to the inter-atomic vectors between Sb shown in Fig. 2.

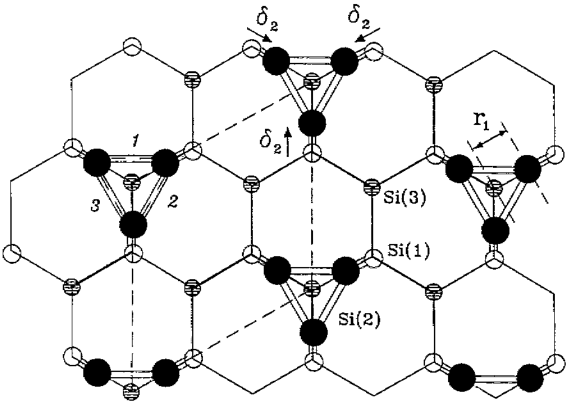

Fig. 2. $(\sqrt{3}\times\sqrt{3})$ surface reconstruction of Sb on Si(111). Solid, hollow and hatched circles represent Sb, the first layer and the second layer of Si atoms, respectively. Lateral displacements from the ideal positions for the first layer of Si atoms are shown. d_{12} for Sb atoms is an absolute distance, not a displacement. Inter-atomic vectors between Sb are also shown corresponding to six peaks in the Patterson function.

Table 1

Displacement parameters used for a least-squares fit. Also shown are thermal vibration amplitudes $\sigma=\sqrt{\langle u^2\rangle}$ for Sb, the first three layers near surface, Si(S), and bulk Si below three layers, Si(B)[a]

	Our work	Ref. [11]	Ref. [13]
r_1	1.688 ± 0.003	1.63	1.63
d_{12}	2.437 ± 0.017	2.51	2.63
δ_2	0.123 ± 0.014	0.06	(−0.18)
δ_4	0.048 ± 0.009	−0.07	–
δ_5	-0.127 ± 0.030	−0.16	–
δ_6	-0.028 ± 0.017	−0.16	–
δ_7	0.027 ± 0.020	−0.10	–
δ_8	-0.011 ± 0.008	−0.10	–
σ_{Sb}	0.25 ± 0.007	–	–
$\sigma_{Si}(S)$	0.15 ± 0.007	–	–
$\sigma_{Si}(B)$	0.08	–	–

[a] Numbers are all in Å units.

for all the atoms in the second (third) Si layers and all three layers were displaced downwards with respect to their ideal positions. The distance between the first and second layers of Si was $d_{23}=0.874$ Å, that between the second and third $d_{34}=2.411$ Å. The second and third layers of Si atoms each have two symmetry-inequivalent atom positions. Fig. 2 shows these sites in the second layer, Si(2), directly below the Sb trimer, and Si(3). Symmetry prevents lateral displacements of these atoms, but their vertical displacements do not need to be the same amount or even in the same direction. So, for the second (third) layer of Si atoms two independent parameters δ_5, δ_6 (δ_7, δ_8) were used for vertical displacements in our fitting model as shown in Fig. 3. Previous experimental results from Ref. [13] and our results are shown next to Mårtensson et al.'s in Table 1. It turned out that the displacements of δ_4 and δ_7

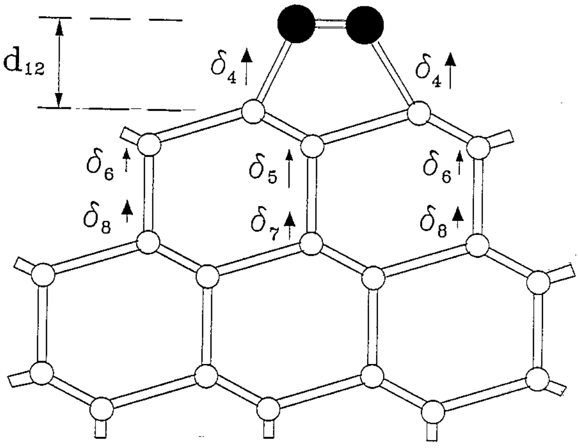

Fig. 3. Side view of Sb adsorbed Si(111). Vertical displacement vectors are shown for the first three layers of Si near surface.

of Si atoms were upward and δ_5, δ_6, δ_8 downward, with $d_{23}=0.918$ Å and $d_{34}=2.266$ Å. With all these displacement parameters, thermal vibration amplitudes of atoms were included in our fitting model and their values are shown in Table 1. In general, the thermal vibration amplitude of surface atoms is bigger in the surface normal direction than in the surface parallel direction, but an anisotropic thermal vibration amplitude in our fitting model did not make any noticeable change in the fit. Therefore, we assumed isotropic thermal vibration amplitudes for all atoms. Our result of thermal vibration amplitude, $\sigma=0.25$ Å, for Sb is a large value but also comparable with those obtained from other cases such as 0.12 Å for Si on Si(111)-(2×1) and 0.16 Å for Sb on Si(100) [19,20].

Fig. 4 shows our experimental results and fits of the integrated intensities along three fractional-

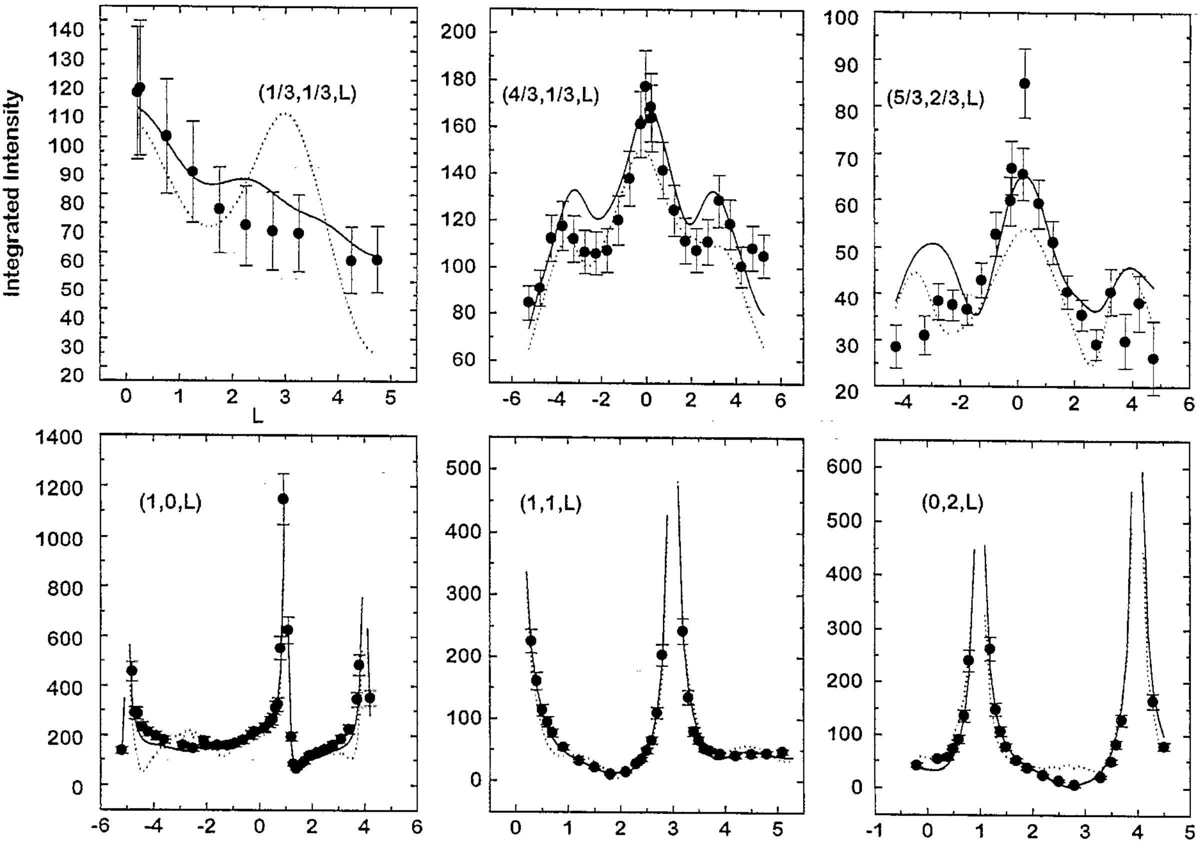

Fig. 4. Integrated intensities of fractional-order and integer-order rods. Solid lines and dotted lines are the best fit for T_4 and H_3 sites, respectively. Note that $l<0$ was obtained from inversion symmetry, $I(-h,-k,-l)=I(h,k,l)$.

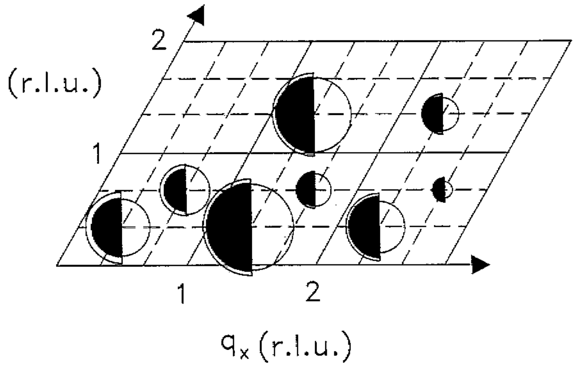

Fig. 5. Integrated intensities of fractional-order in-plane peaks. The radii of solid and hollow semi circles are proportional to measured and calculated integrated intensities, respectively. Experimental errors are represented as outer shells of solid circles.

Table 2
Bond lengths between atoms near surface in Å[a]

	Our work	Ref. [11]	Ref. [13]
Sb–Sb	2.92±0.01	2.82	2.82
Sb–Si	2.47±0.04	(2.57)	2.74
Si(1)–Si(2)	2.30±0.05	–	–
Si(1)–Si(3)	2.44±0.05	–	–

[a] Numbering of Si atoms is shown in Fig. 2. Bulk Si has a bond length of 2.35 Å.

Table 3
Previously measured Sb–Sb bond lengths in Si(100) and Si(111) with different techniques

	Si	Sb–Sb	Ref.
X-ray standing wave	(100)	2.75±0.06	[20]
X-ray standing wave	(100)	2.81±0.09	[21]
SEXAFS	(100)	2.88±0.03	[22]
Ion chanelling RBS	(100)	2.80±0.10	[23]
X-ray diffraction	(100)	2.85±0.01	[24]
LDA cluster theory	(100)	2.93±0.05	[25]
LDA slab theory	(100)	2.96	[26]
SEXAFS	(111)	2.87±0.02	[12]
X-ray diffraction	(111)	2.92±0.01	Our work
LDA theory	(111)	2.82	[11]

order rods and three integer-order rods, and Fig. 5 for the fractional-orders alone. The bond lengths between Sb–Sb, Sb–Si and Si–Si are listed in Table 2. Lateral and vertical displacements of Sb adatoms as well as the first three layers of Si atoms were taken into account. The bond length 2.92 Å between Sb–Sb on Si(111) is a bit larger than the previous determination[13].

There now exist multiple experimental and theoretical determinations of the Sb–Sb bond length on both Si(111), where a trimer is formed, and on Si(100) with a dimer. These are summarized in Table 3. The covalent bonding is very different between the two cases, with 60° angle in the trimer and ca 90° in the dimer. A corresponding trend in bond length might be expected by analogy with inorganic compounds of phosphorus in the same chemical group V: the best example we found was compounds of phosphorus and sulfur which formed molecules with analogous structures to the dimer and trimer. In the P_4S_7 molecule, P is in a very similar geometrical position as Sb on Si(100) and has a P–P bond length of 2.33 Å [27]. On the other hand, in the P_4S_3 molecule, P is in a covalently-bonded trimer, like Sb on Si(111), and has a P–P bond length of 2.24 Å [27]. So, the bond length is actually decreasing from a dimer to a trimer structure. The experimental data for dimer and trimer configurations of Sb (Table 3) do not concur with this apparent trend for P. The almost identical Sb–Sb bond length on Si(100) and Si(111) may be due to metallic behavior, which has been seen in photoemission experiments on Sb/Si(100) [28].

For the integer-order rods, the fit is almost perfect and well describes even the very detailed structures. However, for the fractional-order rods the fit deviates from the data points. Anisotropy of the vibrations was found not to account for the differences; we did not try an anharmonic model, however, so this remains a possibility. We tried many variations in our model to fit the fractional-order rods. The observation of the small peaks along (4/3, 1/3, L) and (5/3, 2/3, L) rods three reciprocal lattice units away from the main peak led us to try a variation in our model by adding more (fractionally occupied) layers of Sb on top of those of the original model. Because Sb is heavier and has about the same spacing as Si, this should produce stronger side peaks. Others were to change the occupancy of the first and second layer of Si atoms or substituted Sb for Si in the first layer, but none of these attempts improved the result.

4. Conclusion

In summary, we studied a Sb adsorbed Si(111) surface using X-ray diffraction. Through the Patterson function the $(\sqrt{3}\times\sqrt{3})$ reconstruction was clearly identified. Detailed atomic displacements down to the third layer of Si were obtained. Contrary to a previous result, the first and half of the third layer of Si atoms were found to move upwards. Even though the thermal vibration amplitude is anisotropic in general, a least-squares fit with isotropic thermal vibration amplitude model was good enough to explain our experimental results.

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