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Surface by X-ray Standing Waves

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# Analysis of the Dimerized Sb/Si(001)-(2×1) Surface by X-ray Standing Waves

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## Abstract

X ray standing wave measurements were undertaken to study the bonding position of Sb adatoms on the Sb-saturated Si(001)-(2×1) surface. Using the (004) and (022) Bragg reflections, we find that the Sb atoms form dimers, and that the center of the Sb ad-dimers lies 1.64 Å above the bulk-like Si(004) surface atomic plane. Our in-plane results are compared to two structural models consisting of dimers whose bonds are parallel to the surface plane and whose centers are either shifted or unshifted (parallel to the dimer bond direction) relative to the underlying substrate planes. We thus find two special cases consistent with our data: one with symmetric (unshifted) dimers having a dimer bond length of 2.81 Å, and the other with midpoint-shifted dimers, having a bond length of 2.88 Å and a lateral shift of 0.21 Å.

## Introduction

The structure and substrate response of the Sb-terminated Si(001) surface have implications for two technologically important phenomena in molecular beam epitaxy (MBE), namely surfactant-mediated epitaxy (SME) and construction of delta-doping layers. Ironically, SME relies on a near-total segregation of surface Sb atoms during growth, while delta-doping requires high incorporation rates. Clearly, understanding of the behavior and geometric structure of the Sb/Si surface is needed to learn under what conditions these nearly contrary requirements may be satisfied. Previous experimental investigations have brought low energy [1-4] and high energy [5,6] electron diffraction, core level spectroscopy [5,6], scanning tunneling microscopy (STM) [1,2,6], surface extended x ray absorption fine structure (SEXAFS) [1], medium energy ion scattering [3] and transmission MeV ion channeling [4] to bear on various aspects of the problem. In addition, the stable bonding site and structure have been calculated using a first principles molecular cluster approach [7]. The picture that has arisen out of these investigations is one where Sb adsorption saturates at nearly one monolayer coverage (1 ML =  $6.78 \times 10^{14}$  cm<sup>-2</sup>) at substrate temperatures above about 350°C. Locally, the well-known clean surface Si dimer reconstruction is lifted, and the adsorbed Sb atoms form new dimers on top of nearly bulk-like Si, similar to the behavior of As atoms on Si(001) [8]. The dimers are arranged in rows, resulting in the familiar (2×1) symmetry. As the pentavalent Sb atoms can form three bonds (and one lone-pair orbital), and the tetravalent, top-layer Si atoms can form four bonds, there are no dangling bonds, and the surface is rather passive [9]. The compressive strain induced by the mismatch in lattice size between Sb and Si, however, appears to cause numerous vacancy and antiphase defects in the Sb overlayer [2]. Thus, the saturation coverage of Sb is somewhat less than a full monolayer, ranging from 0.7 to 0.9 ML, depending on sample temperature and incident Sb species (Sb<sub>4</sub> or Sb<sub>1</sub>) [3]. The breakup of the rows of dimers by defects and the high density of anti-phase boundaries imply a short coherence length for the domains of dimerized Sb. This explains the diffuseness and weakness of the half-order spots observed with electron diffraction [1-5]. One specific issue that has not yet been resolved is whether the Sb ad-dimer is symmetric, or if it is either tilted (as on clean Si(001) [10]) or shifted with respect to the underlying substrate (as on Sb/Ge(001) [11]).

In this paper, we present an x ray standing wave (XSW) investigation of the Sb-saturated Si(001) surface, employing reflections from the (004) and (022) bulk lattice planes. We thereby precisely determine several important Fourier components of the spatial distribution of Sb atoms relative to the Si lattice. We interpret these spatial distribution data in terms of several principal structural models of the Sb/Si(001) surface, and we thereby make (model-dependent) determinations of the Sb-Sb dimer bond length, asymmetric tilt, and midpoint shift. We pay particular attention to the analysis of a dimerized surface with a limited set Fourier components.

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## Experimental Procedure and Results

The experiments were conducted at beamline X15A of the National Synchrotron Light Source at Brookhaven National Laboratory. The details of the experimental procedure were given in a previous publication [12]; the XSW technique as well as the experimental arrangement at X15A have recently been extensively reviewed by Zegenhagen [13]. The Sb-saturated Si(001)-(2×1) surface was prepared using standard procedures. Subsequently, an incident x ray beam from the synchrotron radiation source was collimated and monochromated by a double-crystal monochromator and directed through a Be window into the UHV chamber. The single crystal sample was held at room temperature and placed so that the x ray beam was Bragg-reflected by either the (004) or the (022) set of diffraction planes. We used 6.23 keV x rays for the (004) measurement, and 6.77 keV x rays for the (022) measurement. At each angular step, the reflected x ray intensity and fluorescence spectrum were recorded simultaneously.

Figure 1(a) shows the Si reflectivity and Sb L fluorescence yield (normalized to unity at off-Bragg angles) as a function of the Bragg reflection angle  $\theta$  for the (004) reflection (diffraction vector normal to the sample surface). The solid line through the reflectivity data is a fit to standard dynamical diffraction theory [14]; the line through the fluorescence yield is a fit to a parametrization that will be discussed below. Figure 1(b) shows similar data acquired for the same surface while scanning through the (022) reflection. Note that the (022) diffraction vector is tilted at  $45^\circ$  from the [004] surface normal direction.

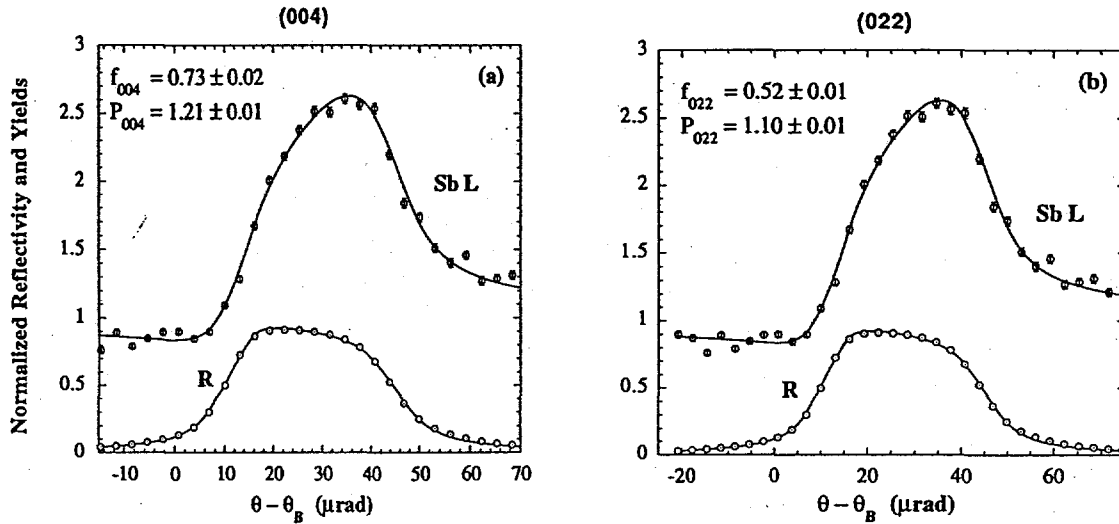


Fig. 1. The experimental and theoretical angular dependence for the x ray reflectivity and Sb L fluorescence yield for: (a) the (004) reflection at  $E_\gamma = 6.23$  keV, and (b) the (022) reflection at  $E_\gamma = 6.77$  keV.

## Discussion

The interference of the coherently coupled incident and Bragg-reflected x ray plane waves generates an XSW in and above the crystal, with the XSW nodal planes parallel to and having the same periodicity as the diffraction planes. The phase of the standing wave with respect to the diffraction planes shifts by  $180^\circ$  as the Bragg angle  $\theta$  is scanned from the low-angle side of the rocking curve to the high-angle side. This phase shift moves the antinodal planes of the standing wave inward by one-half of the d-spacing  $d_{hkl}$ . Thus, the angular dependence of the fluorescence yield  $Y(\theta)$  from an adatom layer can be described as:

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)} f_{c,H} \cos[v(\theta) - 2\pi P_H] , \quad (1)$$

where  $R(\theta)$  is the reflectivity and  $v(\theta)$  is the relative phase of the diffracted plane wave. The coherent fraction  $f_{c,H}$  and coherent position  $P_H$  correspond to the amplitude and phase, respectively, of the  $H$ th Fourier component of the time-averaged spatial distribution of the nuclei of the adatoms (projected into a unit cell).  $H$  is the reciprocal lattice vector for the  $(hkl)$  diffraction planes. More specifically, the coherent fraction can be written as the product of three factors [15]:

$$f_{c,H} = C a_H D_H \quad , \quad (2)$$

where  $C$  is the fraction of adatoms at ordered positions,  $a_H$  is a geometrical factor, and  $D_H$  is the Debye-Waller factor. The Debye-Waller factor can be written as  $D_H = \exp(-2\pi^2 \langle u_H^2 \rangle / d_H^2)$ , where  $\langle u_H^2 \rangle$  is the mean-squared thermal vibrational amplitude of the adatom in the  $H$  direction.

While the information provided by an XSW scan, viz., the coherent fraction and coherent position, is unambiguous and completely model-independent, the process of determining structural parameters from these data is, however, somewhat model-dependent. Each XSW scan measures the amplitude and phase of a single Fourier component of the atomic spatial distribution; many such Fourier components are required to completely describe a complicated structure containing multiple inequivalent adatom sites. Furthermore, it is only possible to use XSW to obtain Fourier components corresponding to strong, bulk diffraction vectors. Without a complete set of Fourier components, therefore, we must make simplifying assumptions and employ symmetry arguments to deduce the structure.

First, let us consider the case of the Sb atoms forming symmetric (*i.e.*, not buckled or shifted) dimers on the Si(001) surface; in that structure, there are two ordered positions equally occupied by Sb atoms. The coherent position  $P_{004}$  equals  $h'/d_{004}$ , where  $h'$  locates the height of the Sb ad-dimer relative to the Si(004) bulk-like atomic plane. Based on symmetry considerations, the value of  $P_{022}$  should equal  $(1+P_{004})/2$  for symmetric dimers. Furthermore, the (004) geometrical factor  $a_{004}$  is unity, while the (022) geometrical factor would be:

$$a_{022} = |\cos(\pi L/2d_{022})| \quad , \quad (3)$$

where  $L$  is the Sb-Sb dimer bond length. The ambiguity in the interpretation of the experimental observables of XSW that was discussed above is essentially contained in the geometrical factor; similar expressions for  $a_H$  can be derived for other structural models. We will consider three other models: one in which the axis of the Sb ad-dimer can be tilted (or buckled) with respect to the Si surface, one in which the midpoint of the dimer can be shifted laterally along the Si surface, and one in which the dimer can be both tilted and shifted. (See Fig. 2) These models are all consistent with the observed electron diffraction patterns. The tilted dimer model is considered here since the clean Si(001)-(2x1) surface is believed to exhibit this geometry [10]. On the other hand, adsorption of Sb onto Ge(001) was found to result in dimers whose midpoints were shifted laterally along the axis of the Sb-Sb bond by 0.16 Å [11]. Although that structure has never been reported for the Sb/Si(001) system, it does not conflict with any published experimental data, and thus seems to be a good candidate for the present system. Finally, we considered a more general model wherein dimers could be both tilted and shifted.

The coherent fractions ( $f_{c,004}$ ,  $f_{c,022}$ ) and coherent positions ( $P_{004}$ ,  $P_{022}$ ) shown in Fig. 1 are determined by  $\chi^2$  fits of Eq. 1 to the Sb L fluorescence data (solid lines in Fig. 1). The measured value of  $P_{004} = 1.21 \pm 0.01$  indicates that the Sb ad-dimer height  $h' = P_{004} d_{004} = 1.64 \pm 0.02$  Å above the Si(004) bulk-like atomic planes. The measured value of  $P_{022}$  is  $1.10 \pm 0.01$ ; the fact that this value is equivalent to  $(1+P_{004})/2$  confirms that the Sb atom *distribution* is symmetrically centered about one of the two-fold symmetry sites of the surface. This would be the case for all of the structural models under consideration here (except the tilted-and-shifted-dimer model), provided the surface was equally populated by rotationally- and translationally-equivalent

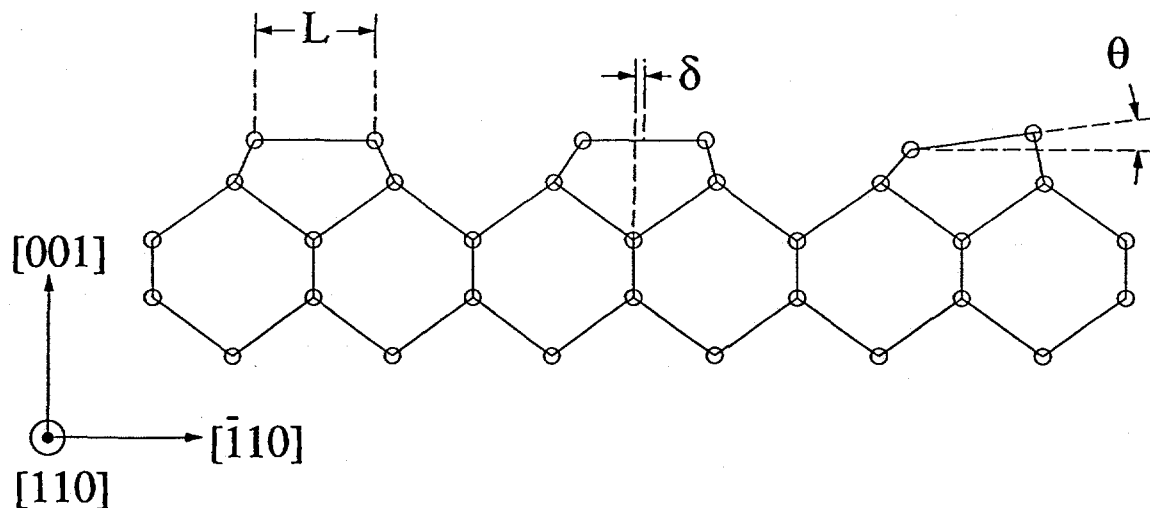


Fig. 2 Side view illustrating the principal structural parameters used to describe the geometry of the Sb ad-dimers in the three models considered.

domains. Furthermore, the level of symmetry-breaking of the distribution introduced by the tilted-and-shifted-dimer model is comparable to our experimental uncertainty, so we will not rule that model out based on the value of  $P_{022}$  alone.

In a SEXAFS experiment, Richter *et al.* [1] measured the Sb-Si and Sb-Sb bond lengths for this surface system, finding a Sb-Si bond length of  $2.63 \pm 0.04 \text{ \AA}$  and a Sb-Sb bond length of  $2.88 \pm 0.03 \text{ \AA}$ . Assuming a symmetric dimer geometry, the SEXAFS values imply that the Sb ad-dimer resides  $1.74 \pm 0.05 \text{ \AA}$  above the surface Si plane. (Allowing a midpoint shift of  $0.2 \text{ \AA}$  [see below] causes this calculated height to decrease by approximately  $0.02 \text{ \AA}$ .) Our XSW measurements indicate that the center of the Sb ad-dimer is located  $1.64 \pm 0.02 \text{ \AA}$  above the Si(004) bulk-extrapolated lattice planes. Therefore, we can conclude that at room temperature the top layer Si atoms on the saturated Sb/Si(001)-(2 $\times$ 1) surface are relaxed inward by  $0.10 \pm 0.05 \text{ \AA}$ . This relaxation was the subject of a previous publication [12].

Besides the height of the center of the dimers above the Si(004) planes, which depends only on the value of  $P_{004}$ , there are three other structural parameters necessary to describe the most general dimer geometry considered here. These are  $L$ , the dimer bond length,  $\theta$ , the tilt angle of the dimer from the surface plane, and  $\delta$ , the lateral shift of the dimer along its axis [11], as illustrated in Fig. 2. In addition, one must know or calculate the ordered fraction  $C$  and the Debye-Waller factor (or the thermal vibrational amplitude  $\sqrt{\langle u_H^2 \rangle}$ ) for the Sb adatoms. Thus, we have up to five remaining unknown quantities, compared to three remaining equations (those for  $F_{004}$ ,  $P_{022}$ ,  $F_{022}$ ). We must therefore make some simplifying assumptions about two of the five remaining structural parameters. We will start by considering the vibrational amplitude.

The ion channeling study reported a thermal vibration amplitude of  $\sqrt{\langle u_H^2 \rangle} = 0.25 \pm 0.1 \text{ \AA}$  for the Sb atoms on this surface at room temperature [4]. However, our XSW measured value of  $f_{c,004} = 0.73 \pm 0.02$  implies that the maximum possible value for  $\sqrt{\langle u_{004}^2 \rangle}$  is  $0.18 \text{ \AA}$ . For our calculations of the remaining structural parameters (only), we will assume the thermal vibrational amplitude of Sb on the Sb/Si(001)-(2 $\times$ 1) surface at room temperature to be isotropic and equal to  $0.12 \pm 0.02 \text{ \AA}$ . This value agrees with the theoretical prediction calculated for the clean Si(001)-(2 $\times$ 1) surface [16]. Also, it is close to the room-temperature value inferred indirectly using XSW for the case of As/Si(001)-(2 $\times$ 1) [17]. Using this  $\sqrt{\langle u_H^2 \rangle}$  value, the Debye-Waller factors are  $D_{004} = 0.86 \pm 0.04$  and  $D_{022} = 0.93 \pm 0.02$ .

To calculate the parameters for the most complicated (and therefore general) model, the tilted-and-shifted-dimers model, we chose to assume that the Sb-Sb bond length  $L = 2.88 \pm 0.03 \text{ \AA}$  determined by SEXAFS [1] was correct. We could then determine  $C$ ,  $\theta$  and  $\delta$ . Using this

value for  $L$ , the solution consistent with our results was one in which  $\theta$  was vanishingly small, making this structure degenerate with the shifted-dimers model. Furthermore, if  $\delta$  was held at zero, then there was no value of  $\theta$  that could provide a consistent solution to our results. Thus, a structure containing any tilting of the dimers is not consistent with our measurements. The same conclusion was reached in the ion-channeling study [4]. We will not consider further this class of structural model.

It appeared that we could then consider the shifted-dimers model, and determine  $C$ ,  $L$  and  $\delta$  from the remaining three equations. However, the equation for  $P_{022}$  involves  $\delta$  only if both it and  $\theta$  are non-zero. Since  $\theta$  was shown to vanish, we have only two remaining equations and three unknowns. The best employment of our observed data, then, is to solve for a family of solutions of involving  $L$  and  $\delta$  by determining  $C$  from the data and plotting all  $(L, \delta)$  pairs consistent with our data. This is principally determined by the (022) geometrical factor, which for this model becomes:

$$a_{022} = |\cos(\pi L/2d_{022}) \cos(\pi\delta/d_{022})| \quad (3)$$

The result is shown in Fig. 3, which plots midpoint shift  $\delta$  as a function of bond length  $L$ . In such a plot, the symmetric-dimers model is just a special case represented by the point where  $\delta$  is equal to zero. For this case, the value of  $L$  was found to be  $2.81 \pm 0.08 \text{ \AA}$ . Note that this value is significantly shorter than that measured by SEXAFS [1]. The value of  $\delta$  dictated by our data grows rapidly for increasing values of  $L$  above this point. Another important point in the family of solutions (dashed lines in Fig. 3) is the point where  $L$  is equal to that found by SEXAFS [1]. If this bond length ( $2.88 \text{ \AA}$ ) is correct, then our results imply that the dimers must have a midpoint shift of  $0.21 \pm 0.10 \text{ \AA}$ . This interesting structure has never before been reported for a Group V/Si(001)-(2x1) surface system.

Although it is not possible for us to conclude on the basis of the present data alone which allowed  $(L, \delta)$  point is correct, we favor the symmetric-dimers model (*i.e.*,  $\delta = 0$ ) based on its simplicity and on chemical reasoning. Our value for the bond length  $L$  barely agrees within experimental uncertainty with the value measured by SEXAFS ( $2.88 \pm 0.03 \text{ \AA}$ ) [1] or predicted by theoretical calculation ( $2.93 \text{ \AA} \pm 0.05 \text{ \AA}$ ) [7]. Our value is, however, in good agreement with that determined by ion channeling ( $2.8 \pm 0.1 \text{ \AA}$ ) [4]. In our study, the principal contribution to the relatively large uncertainty ( $0.08 \text{ \AA}$ ) in the dimer bond length comes from our uncertainty in assuming a value for the Sb thermal vibrational amplitude. In the future, we will use higher-order harmonic XSW measurements [15] on this surface to determine additional Fourier components of the atomic distribution. With those data, we expect to be able to determine which of the structural models consistent the present data is the correct one. Also, we can thus directly and more precisely measure the thermal vibration amplitudes  $\sqrt{\langle u_{004}^2 \rangle}$  and

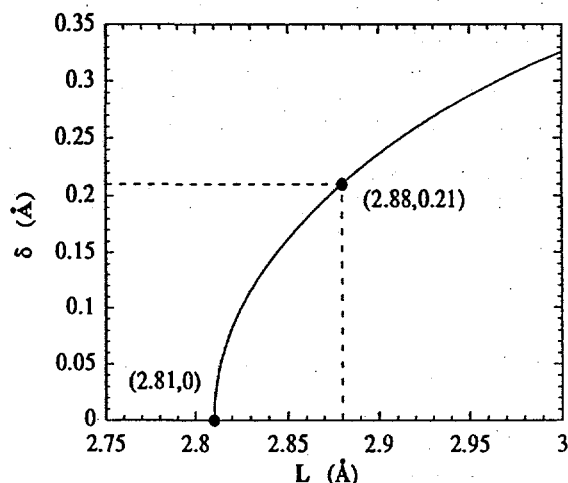


Fig. 3. Family of solutions of dimer bond length  $L$  and midpoint dimer shift  $\delta$  consistent with present data. A vibrational amplitude of  $0.12 \pm 0.02 \text{ \AA}$  was assumed for the calculation.

$\sqrt{\langle u_{022}^2 \rangle}$ , and hence reduce uncertainties in our Sb-Sb bond length measurements. We eventually plan to use this method to directly study the behavior of adatom thermal vibrations on the Si(001)-(2x1) surface at various temperatures.

## Conclusions

We have measured the position of Sb atoms on the saturated Sb/Si(001)-(2x1) surface using the XSW technique. We find that Sb atoms occur as dimers whose centers are located  $1.64 \pm 0.02$  Å above the bulk-like Si lattice plane. Our data are consistent with the class of structures having dimers whose midpoints may be shifted or unshifted parallel to the dimer bond direction. Tilted (or buckled) dimers are inconsistent with our findings. This work either demonstrates a structure never before reported for any Group V/Si(001)-(2x1) surface (shifted dimers), or it indicates that the Sb-Sb dimer bond length is significantly shorter than previously reported. Our measurements will be important in establishing a structural baseline for our upcoming experiments using Sb during Surfactant-mediated epitaxy and construction of delta-doping layers, as well as for a stringent test of predictive theoretical calculations.

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