

High-resolution structural analysis of the Sb-terminated GaAs(001)-(2×4) surface

T.-L. Lee

Department of Materials Science and Engineering and Materials Research Center, Northwestern University, Evanston, Illinois 60208

M. J. Bedzyk

*Department of Materials Science and Engineering and Materials Research Center, Northwestern University, Evanston, Illinois 60208
and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

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The precise locations of Sb atoms for the GaAs(001):Sb-(2×4) surface were measured by the x-ray standing-wave (XSW) technique. The XSW results are consistent with symmetric Sb dimers, whose formation has recently been predicted by four competing models. The (004) and (022) XSW analysis determined the Sb dimer height and bond length to be 1.72 and 2.84 Å, respectively. The Sb coverage of the (2×4) reconstruction was measured by Rutherford backscattering to be 0.48 monolayers. This coverage agrees with the two proposed structural models that have two Sb dimers per (2×4) unit cell and disagrees with the models that propose one or three Sb dimers. Finally, a (111) XSW measurement, which tested for lateral displacement of the Sb dimers in the [110] direction, was used to discriminate between the remaining two models. [S0163-1829(98)50824-7]

The atomic arrangement at compound semiconductor surfaces and interfaces is closely related to the initial growth of the corresponding strained layer heterostructures. Such structures have potentially broad applications in telecommunication and high-speed electronic components. Scientifically, there has been a growing interest in the (001) III-V surfaces, arising from the abundant, strongly coverage-dependent surface structures. For GaAs(001), for instance, extensive investigations have been carried out, and the surface has been reported to exhibit various phases ranging from the most As-rich $c(4\times 4)$ to the most Ga-rich (4×6) reconstruction.¹

Recently, similar structures were observed by Madea *et al.*² on a Sb-terminated GaAs(001) surface. Their reflection high-energy electron diffraction (RHEED) study revealed a number of different phases, including a (2×4) pattern for annealing temperatures between 440 °C and 560 °C. Their core-level photoelectron spectroscopy measurements suggested that this (2×4) reconstruction was formed by the surface Sb bonding to the underlying Ga after the desorption of As at the Sb/GaAs interface. Later, Esser *et al.*³ performed a reflectance anisotropy spectroscopy (RAS) study combined with total-energy and tight-binding calculations. Their calculations rendered a Sb dimer bond length of 2.86–2.87 Å, and the RAS result was used in discriminating between several possible (2×4) models. Meanwhile, Moriarty *et al.*⁴ reported a scanning tunneling microscopy (STM) investigation on a number of Sb-induced reconstructions on GaAs(001). Their study showed considerable differences in the structure and ordering of the Sb- and As-terminated GaAs(001)-(2×4) surfaces.

The bonding geometry of the Sb/GaAs(001) (2×4) surface was first addressed quantitatively by Sugiyama *et al.*⁵ using back reflection x-ray standing waves (BRXSW). By monitoring the Sb 3*d* photoelectron yields through the GaAs (111) and $(\bar{1}\bar{1}\bar{1})$ Bragg reflections, they reported a Sb dimer height of 1.81 Å and a dimer bond length of 2.95 Å. These

values are notably larger than other related measurements^{6–8} and theoretical calculations³ of Sb dimers on semiconductor surfaces.

Herein we report a conventional x-ray standing-wave study of the GaAs(001):Sb-(2×4) surface. By measuring the Sb *L* fluorescence yields for the bulk GaAs (004) and (022) reflections at a conventional Bragg geometry, we have a more direct measure of the dimer height and dimer bond length than that given by the {111} BRXSW measurements. Our values are consequently a more accurate test for the theoretical calculations.³ In addition, we used a (111) XSW measurement [in combination with the (004) and (022)] to look for a lateral surface relaxation that was predicted in one of the surface models proposed by Esser *et al.*³ and favored by their RAS results. We also determined the Sb coverage of the (2×4) surface using Rutherford backscattering spectrometry (RBS) and compared these results with the previously proposed (2×4) models, which vary in Sb coverage from 0.25 to 0.75 ML. The final synthesis of our measurements and analysis will be shown to be consistent with one and only one of the four competing models for this surface structure.

The GaAs(001) substrate was prepared prior to the XSW measurement with a 1- μ m-thick homoepitaxial layer. The surface was then protected by an amorphous As layer for sample transfer in air. The XSW experiments were conducted at beamline X15A of the National Synchrotron Light Source at Brookhaven National Laboratory. The UHV facility at X15A (Ref. 9) (base pressure $\sim 9\times 10^{-11}$ torr) consists of a molecular-beam-epitaxy (MBE) system coupled with a low-energy electron diffraction/Auger electron spectroscopy (LEED/AES) chamber and an XSW chamber, allowing sample preparation and *in situ* surface characterization. After introduction into the MBE system, the GaAs substrate was first degassed at 250 °C for about 45 min. The As protective layer was then removed by thermal desorption at 350 °C and a $c(4\times 4)$ LEED pattern was observed. The

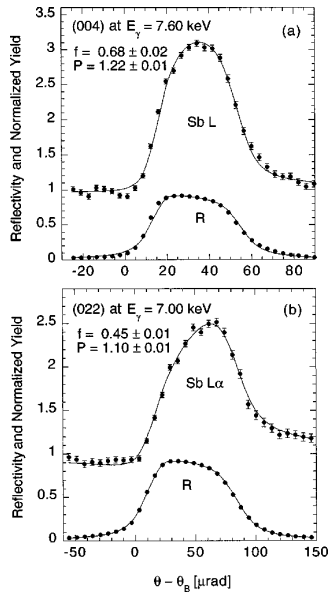


FIG. 1. The GaAs(001):Sb-(2×4) experimental XSW data (filled circles) and the best fits (solid lines) for the normalized Sb L fluorescence yields and the reflectivities R versus the incident angle θ for the GaAs (a) (004) and (b) the (022) Bragg reflections.

As-rich (2×4)/ $c(2\times 8)$ reconstructed surface was attained by annealing the sample further at 400°C – 450°C . Sb was deposited from a Knudsen cell held at 420°C . The deposition rate was calibrated to be ~ 0.7 ML/min by measuring the Sb MNN Auger peak intensities from a Sb-terminated Si(001) surface which is known to have a saturated coverage at 0.8 ML.¹⁰ To prepare the Sb-terminated GaAs(001) surface, ~ 4 ML of Sb was deposited with the substrate held at room temperature (RT), followed by a 20-min anneal at 505°C . The LEED pattern showed a clear (2×4)/ $c(2\times 8)$ reconstruction with streaky half-order spots along the [110] direction. The fourfold spots were much sharper than those from the As-rich clean surface, indicating a more highly ordered surface had developed upon the adsorption of Sb. This observation is consistent with the significantly lower density of kink sites on the Sb-terminated surface reported by STM.⁴

X-ray standing-wave measurements were then used to triangulate the Sb atomic positions relative to the GaAs lattice. Each XSW measurement involves scanning the incident x-ray energy (equivalent to scanning the angle of the sample) through a particular GaAs hkl Bragg reflection. During these eV-wide scans, the phase of the standing-wave shifts by 180° with respect to the hkl diffraction planes. Thus, the electric-field intensity experienced by the adsorbate layer is modulated. With an incident photon energy E_γ above the Sb L_{III} edge, the induced modulation of the Sb L fluorescence yield is monitored by a solid-state Si(Li) detector. To locate the Sb positions, we employed the GaAs (004) reflection at $E_\gamma = 7.60$ keV to directly measure the Sb dimer height (h'), and the (022) reflection at $E_\gamma = 7.00$ keV to deduce the dimer bond length L .

Figures 1(a) and 1(b) show the results of these two measurements. Based on dynamical diffraction theory, the angular dependence of the fluorescence yield from an adsorbate can be described as

$$Y(\theta) = Y_{\text{OB}} \{1 + R(\theta) + 2\sqrt{R(\theta)} f_{\text{H}} \cos[\nu(\theta) - 2\pi P_{\text{H}}]\}, \quad (1)$$

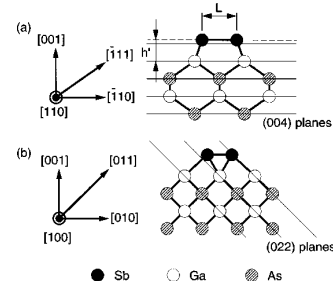


FIG. 2. The (a) [110] and (b) [100] projections of an Sb-terminated GaAs(001) surface. The solid lines are the atomic planes for the different Bragg reflections. L is the Sb-Sb bond length. h' is the height of the Sb dimer relative to the unrelaxed GaAs(001) surface Ga planes.

where Y_{OB} is the off-Bragg fluorescence yield, $R(\theta)$ is the reflectivity, and $\nu(\theta)$ is the phase of the standing wave (see Ref. 9 for a review of the XSW technique). The coherent fraction f_{H} and the coherent position P_{H} are the amplitude and phase, respectively, of the H th Fourier component of the time-averaged spatial distribution of the adatoms. In simple terms, f_{H} and P_{H} measure the width and the average position, respectively, of the atomic distribution along the H direction. From the χ^2 fits of Eq. (1) to the data in Figs. 1(a) and 1(b), we determined the coherent fractions and the coherent positions to be $f_{004} = 0.68 \pm 0.02$, $P_{004} = 1.22 \pm 0.01$, $f_{022} = 0.45 \pm 0.01$, and $P_{022} = 1.10 \pm 0.01$.

If a symmetric Sb dimer model is assumed, the measured (004) coherent position can be directly related to the dimer height [Fig. 2(a)] by

$$h' = P_{004} d_{004}, \quad (2)$$

which locates the Sb dimer at $h' = 1.72 \pm 0.02$ Å above the last bulk-extrapolated GaAs (004) atomic plane. When compared with the height of Sb dimers formed on a Si(001) surface, which has been measured previously by XSW (Ref. 6) ($h' = 1.64$ Å) and by ion channeling¹¹ ($h' = 1.63$ Å), our result shows that h' is about 0.09 Å higher for Sb on GaAs(001). This is consistent with the fact that Ga has a 0.09 Å larger covalent radius ($r_{\text{Ga}} = 1.26$ Å, $r_{\text{Si}} = 1.17$ Å). In comparison, the determined Sb dimer height on GaAs(001) reported by Sugiyama *et al.* using BRXSW (Ref. 5) ($h' = 1.81 \pm 0.02$ Å) is 5% larger than our measured value.

Notice that the measured coherent positions satisfy the following relationship:

$$P_{022} = (1 + P_{004})/2. \quad (3)$$

This meets the requirement for adatoms occupying twofold symmetry related positions around the bridge site on a GaAs(001) surface [Fig. 2(b)]. In addition, the fact that the measured coherent fraction f_{022} is significantly lower than f_{004} is also consistent with the Sb symmetric dimer model, since the positions of the dimerized Sb atoms in such a model are equivalent along the [004] direction [Fig. 2(a)] but inequivalent along the [022] [Fig. 2(b)]. To extract the Sb-Sb bond length L from the two measurements, the coherent fraction is decomposed into a product of three factors based on the convolution theorem

$$f_{\text{H}} = C a_{\text{H}} D_{\text{H}}, \quad (4)$$

where C is the fraction of adatoms at ordered positions, D_{H} is the adatom Debye-Waller factor, and a_{H} is the geometrical factor, accounting for the reduction of the coherent fraction

TABLE I. Theoretical and experimental values of the structural dimensions for the Sb dimers on different surfaces. L is the Sb dimer bond length. h' is the height of the Sb dimer relative to the surface GaAs (004) planes (see Fig. 2).

Substrate	Si(001)	Ge(001)	GaAs(110)	GaAs(001)	GaAs(001)	GaAs(001)
	XSW ^a	XRD ^b	XRD ^c	BRXSW ^d	Theory ^e	Present XSW
h' (Å)	1.64±0.02			1.81±0.02		1.72±0.02
L (Å)	2.75±0.06	2.90	2.80	2.95±0.06	2.86–2.87	2.84±0.05

^aReference 6.

^bReference 7.

^cReference 8.

^dReference 5.

^eReference 3.

due to multiple adatom positions along the \mathbf{H} direction. As illustrated in Fig. 2, it can be shown that $a_{004}=1$ and $a_{022} = |\cos(\pi L/2d_{022})|$. By combining the (004) and (022) results, the dimer bond length L can be determined as

$$L = \frac{2d_{022}}{\pi} \cos^{-1} \left(-\frac{f_{022}D_{004}}{f_{004}D_{022}} \right). \quad (5)$$

At this point, we will make the simplifying approximation that the Sb adatoms have the same RT Debye-Waller B factor as reported for bulk GaAs ($B=0.59 \text{ \AA}^2$),¹² and thus $D_{\mathbf{H}} = \exp(-B/2d_{\mathbf{H}}^2)$ will be estimated as $D_{004}=0.86$ and $D_{022}=0.93$. The two measurements therefore determine the Sb-Sb bond length through Eq. (5) to be $L=2.84 \pm 0.05 \text{ \AA}$, which is in excellent agreement with the first-principles total-energy calculation by Esser *et al.*³ ($L=2.86\text{--}2.87 \text{ \AA}$). Our measured $L_{\text{Sb-Sb}}$ is also very close to the bond lengths of the Sb dimers formed on a GaAs(110) surface⁸ ($L=2.80 \text{ \AA}$) and on a Ge(001) surface⁷ ($L=2.90 \text{ \AA}$) reported by x-ray diffraction (XRD). While it is about 0.1 \AA longer than the Sb-Sb bond length of a Sb-terminated Si(001) surface measured by XSW (Ref. 6) ($L=2.75 \text{ \AA}$). The BRXSW study by Sugiyama *et al.*,⁵ however, reported a Sb-dimer bond length of $2.95 \pm 0.06 \text{ \AA}$ on the GaAs(001) surface; note that this value is 4% larger than the present measurement, consistent with their report of a 5% larger value of h' .

Since the thermal vibrational amplitude is normally larger for surface atoms, our extrapolated value of $L=2.84 \text{ \AA}$ represents an upper bound on the true Sb dimer bond length. Based on previous XSW measurements for As,¹³ Sb,⁶ and Bi (Ref. 14) dimers on Si(001), we can reasonably approximate that the Sb thermal vibrational amplitude on GaAs(001) should be 0.15 \AA . This value, which is 23% larger than that for bulk GaAs at RT, leads to a reduction in $L_{\text{Sb-Sb}}$ from 2.84 to 2.81 \AA . This small reduction in $L_{\text{Sb-Sb}}$ is included within the quoted $\pm 0.05 \text{ \AA}$ error. We summarize our results in conjunction with other related measurements in Table I.

In addition to measuring the local bonding geometry of the Sb dimer, we also determined the Sb coverage Θ of the (2×4) surface using RBS. Major differences in Sb coverage can be found among the previously proposed (2×4) models: Maeda *et al.*² proposed a model consisting of three Sb dimers per (2×4) unit cell, the theoretical calculations and RAS result by Esser *et al.*³ were in favor of a (2×4) model with two Sb dimers (and two Ga dimers) per unit cell, and the STM study by Moriarty *et al.*⁴ suggested only one Sb dimer per unit cell. These three different (2×4) models correspond to Sb coverages of 0.75, 0.50, and 0.25 ML, respectively. Our RBS result showed that the same sample we stud-

ied with XSW was covered by $3.0 \times 10^{14} \text{ Sb cm}^{-2}$, which is equivalent to 0.48 ML on a GaAs(001) surface ($1 \text{ ML} = 6.26 \times 10^{14} \text{ atoms/cm}^2$). By considering the ordered fraction C measured from the (004) reflection of $C = f_{004}/D_{004} = 0.79$, we can obtain an ordered coverage of $C\Theta = 0.38 \text{ ML}$. This value indicates that under the present growth condition the (2×4) ordered structure was formed by about 0.4 ML of Sb adatoms. This result is consistent with a surface composed predominantly of two Sb dimers per unit cell as proposed by Esser *et al.*³ The ordered coverage of 0.4 ML rules out the possibility that the model proposed by Moriarty *et al.*⁴ with one Sb dimer per unit cell is the only ordered structure on the (2×4) surface ($C\Theta \leq 0.25 \text{ ML}$ for this case).

In Esser's total-energy calculation³ there are two different models considered which have two Sb dimers per (2×4) unit cell. As illustrated in Fig. 3, model I has two Ga dimers in the second layer, and model II has one As dimer in the third layer. The former was based on the clean GaAs(001)- (2×4) α phase proposed by Farrell and Palmstrom,¹⁵ and the latter was based on the GaAs(001)- (2×4) model proposed by Chadi¹⁶ (known as the β_2 phase). Energetically, Esser's calculations show that both model I and II are stable (2×4) structures. The theoretical calculation by Northrup and Froyen¹⁷ show that for the clean (2×4) α phase, the As and Ga atoms in the top two layers will undergo large lateral displacements ($0.4\text{--}1.2 \text{ \AA}$) in the $[110]$ direction to allow the formation of the second-layer Ga-Ga dimers. A similar re-

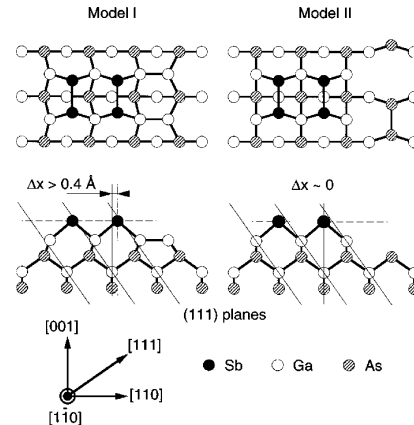


FIG. 3. The top and the $[\bar{1}10]$ side views of two different GaAs(001):Sb- (2×4) models (Ref. 3). Both models have two Sb dimers per unit cell. Model I has two Ga dimers in the second layer and model II has one As dimer in the third layer. Δx in model I is the lateral shift of the Sb dimers along the $[110]$ direction relative to a bulk twofold axis, in response to the strain induced by the formation of the Ga dimers.

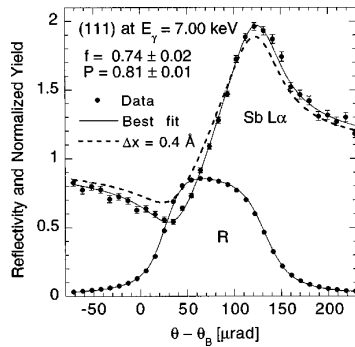


FIG. 4. The (111) XSW data (filled circles) and the best fits (solid lines) for the normalized Sb L fluorescence yield and the GaAs(111) reflectivity R . The dashed line is the calculated Sb fluorescence yields for $\Delta x = 0.4 \text{ \AA}$ in Fig. 3, while the best-fit solid line corresponds to $\Delta x = 0.0$.

laxation effect would be expected to occur on the Sb-terminated surface to accommodate the lateral strain if Sb and Ga dimers coexist in the top two layers as depicted in model I. Since the proposed displacement is perpendicular to the Sb-Sb dimer bonds, the standing wave generated by the (111) reflection would be most sensitive to this effect. Based on symmetry, the surface should be equally occupied by domains with Sb dimers shifted in the $[110]$ and $[\bar{1}10]$ directions. Thus the distribution of Sb atoms from both domains, as projected into one unit cell, should remain centered along a bulk twofold axis. Therefore

$$P_{111} = (P_{004} + 2)/4, \quad (6)$$

which predicts $P_{111} = 0.81$ from our measured value for P_{004} . The proposed lateral relaxation of the surface in model I would broaden the Sb distribution along the $[110]$ direction and lead to a lower (111) coherent fraction. We can calculate this reduction of f_{111} through Eq. (4) with the following formula for a_{111} :

$$a_{111} = |\cos[(4\pi\Delta x/\sqrt{6}d_{111})]|. \quad (7)$$

Here we assume that all Sb dimers are shifted by the same amount, Δx (Fig. 3), along the $[110]$ in either direction. For the purpose of testing the two different models, it would be reasonable to choose in model I a displacement of $\Delta x = 0.4 \text{ \AA}$, which is the lower bound of the lateral shifts calculated for the GaAs(001) (2×4) α phase reported in Ref. 16. This would reduce the (111) geometric factor to $a_{111} = 0.81$ and the coherent fraction to $f_{111} = CD_{111}a_{111} = 0.62$ (with $D_{111} = 0.97$). For model II, the Sb dimers are close to

the ideal positions ($\Delta x \approx 0$), therefore $a_{111} = 1$ and Eq. (4) renders $f_{111} = 0.77$.

Figure 4 shows the result of the (111) XSW measurement carried out at $E_\gamma = 7.00 \text{ keV}$. The Sb coherent position (0.81 ± 0.01) agrees with the symmetry requirement of Eq. (6), while the measured coherent fraction (0.74 ± 0.02) implies $a_{111} \approx 1$ (or $\Delta x \approx 0$), in favor of the structural model without Ga dimers in the second layer (model II). The disagreement of our measurement with model I is evident in Fig. 4 from the difference between the best fit curve (solid line) and the calculated curve for $\Delta x = 0.4 \text{ \AA}$ (dashed line).

In summary, the GaAs(001):Sb- (2×4) surface prepared by MBE was studied by (004), (022), and (111) x-ray standing waves. All three XSW measurements are consistent with the formation of symmetric Sb dimers above the modified bridge site. The Sb dimer height was determined to be $h' = 1.72 \pm 0.02 \text{ \AA}$ above the bulklike (004) Ga atomic plane. The Sb dimer bond length was measured to be $L = 2.84 \pm 0.05 \text{ \AA}$. Both values are in good agreement with previous theoretical calculation and other related measurements. The Sb coverage of the (2×4) reconstruction was determined by Rutherford backscattering to be 0.48 ML, consistent with surface models having two Sb dimers per (2×4) unit cell, and disagreeing with models having one and three Sb dimers per unit cell. Finally, the (111) measurement showed no lateral shift of the Sb dimers in the $[110]$ direction. Referring to the surface models of Esser *et al.*³ shown in Fig. 3, our analysis strongly favors the 2×4 model with one As dimer in the third layer (model II) over the model with two Ga dimers in the second layer (model I).

Note added in proof. A recent first-principles pseudopotential calculation¹⁸ presents an additional model (δ_2) for the 0.5-ML Sb/GaAs(001)- (2×4) surface. However, the large lateral displacement ($\sim 0.6 \text{ \AA}$) along the $[110]$ direction of the Sb dimers in the top layer of this model is inconsistent with our (022) and (111) XSW measurements.

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