

Geometric structure of the Si(111):As-1×1 surface

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Medium-energy ion scattering has been used to study the structure of the Si(111):As-1×1 surface. The results are consistent with a surface model containing threefold-coordinated arsenic atoms in a substitutional first-layer site. A comparison of channeling and blocking data with Monte Carlo simulations shows an 0.24-Å expansion of the arsenic layer from unrelaxed bulk terminated silicon positions (30% of the bulk terminated first-to-second-layer spacing) and an arsenic one-dimensional vibration amplitude of 0.14 Å.

Recently, Olmstead *et al.* reported that the Si(111)-7×7 reconstruction could be removed by terminating the Si(111) surface with arsenic.¹ Total energy calculations and the comparison of band-structure calculations to angle-resolved photoemission measurements² suggest that the first monolayer (ML) of silicon is replaced by 1 ML of arsenic as shown in the inset of Fig. 1. This model of the As-terminated surface is interesting because it is predicted by simple considerations of valence-bond theory; the valency of As allows each arsenic atom to bond to three second-layer silicon atoms, eliminating all surface dangling bonds and leaving a single As lone pair orbital protruding into the vacuum. The Si(111)-7×7 reconstruction arises from the reduction in the number of dangling bonds by reordering surface atoms with a minimum amount of surface and subsurface strain. In contrast, there is no driving force for further reconstruction of the Si(111):As-1×1 surface since the lone-pair electrons are energetically stable, and we are left with a 1×1 surface. This surface is also found to be extremely resistant to surface contamination.

In this Rapid Communication, we present a medium-energy ion-scattering (MEIS) study of the Si(111):As-1×1 surface. The energy dependence of the silicon surface peak was measured along the $[\bar{1}\bar{1}\bar{1}]$ normal and [001] off-normal directions, surface blocking curves were measured near the $[11\bar{1}]$ off-normal direction, and quantitative measurement of the arsenic coverage was obtained for the well-ordered Si(111):As-1×1 surface. The results are consistent with the general model of Ref. 1 in which the As layer occupies substitutional sites on the first layer of an unreconstructed 1×1 surface. A detailed model is presented with the arsenic layer relaxed outward with respect to bulk Si positions by 0.24 Å with a one-dimensional vibration amplitude of 0.14 Å.

The ion-scattering measurements were performed in an ultrahigh-vacuum (UHV) system equipped with a low-energy electron-diffraction (LEED) system, apparatus for Auger analysis, a high-resolution toroidal electrostatic ion energy analyzer ($\Delta E/E = 4 \times 10^{-3}$), and connected to the beam line of a 200-keV ion accelerator.³ The principles of surface-structure determination by MEIS are well described in Refs. 4 and 5.

In order to obtain accurate As coverages and Si surface peak yields, an antimony-implanted standard was used to

calibrate the efficiency of the electrostatic analyzer. The Sb atomic areal density had previously been calibrated to $\approx 2\%$ accuracy by comparison with a known implanted standard.⁶ Scattering yields from As or Si could then be converted to accurate atomic areal densities since the scattering cross sections follow the well-known Rutherford cross section with a small screening correction. Since the electrostatic analyzer does not detect neutral particles, it was necessary to correct for the fraction of neutral particles scattered from the surface. The fraction of neutral particles was measured by means of a solid-state detector equipped with electrostatic deflection plates. At 180-keV proton energy, this fraction was $< 3\%$ and was not a major source of error in the measurement.

The Si(111) samples, 7 mm×20 mm×0.3 mm, *n*-type (phosphorus, 10 Ω cm), were chemically oxidized by the Shiraki method⁷ and subsequently annealed resistively in a UHV preparation chamber by direct current to 850°C to remove the surface oxide layer. Sharp 7×7 LEED patterns were consistently obtained by this procedure. The clean 7×7 surfaces were held at 850°C for 1 min while the As₄ molecular source was heated up to its deposition temperature of 230°C and the background pressure in the preparation chamber rose from 1×10^{-10} to 1×10^{-6} Torr. The sample was then cooled to 600°C and lowered in front of the As₄ source for 1 min, and cooled to 350°C for 3 min before turning off the As₄ beam. The pressure at the sample during this time was 10^{-4} – 10^{-5} Torr. After cooling, the samples were transferred under UHV into the main experimental chamber.

A sharp Si(111):As-1×1 LEED pattern was consistently obtained using this procedure and the arsenic coverage was measured to be 0.93 ± 0.04 ML. the C-KLL/Si-LVV ratio was initially $< 5 \times 10^{-3}$ but was observed to increase slightly after the sample had been exposed to a background pressure of 1×10^{-10} Torr for several hours, saturating at < 0.1 ML carbon. We note that no oxygen KLL line was observed above the background level of the analyzer. Furthermore, no further significant contamination was found after a 5-min exposure to air at 1 atm. *This unusual stability with respect to surface contamination is strongly indicative of saturation of all surface bonds. Samples prepared under somewhat different conditions that exhibited only slightly higher channeling surface peak intensities were much less resistant to con-*

tamination.

The energy dependence of the silicon surface peaks was measured along the $[\bar{1}\bar{1}\bar{1}]$ normal direction in single alignment so that only channeling and not blocking effects need to be taken into account, and the scattered ions were detected at an angle of 110° with respect to the incident beam (open squares in Fig. 1). The dashed line is a computer simulation for an unreconstructed $\text{Si}(111)\text{-}1\times 1$ surface in which all atoms in the crystal were assumed to vibrate independently with Gaussian probability distributions for the x , y , and z displacements. A Si one-dimensional, root-mean-square, isotropic thermal vibration amplitude of 0.075 \AA was used in the simulation (bulk Debye temperature of 543 K), with no enhancement of surface vibrations. In the case of isotropic thermal vibrations, the two-dimensional, root-mean-square thermal vibration amplitude normal to the ion beam is $\sqrt{2}$ times the one-dimensional vibration amplitude. It can be seen from Fig. 1 that the data (open squares) are lower than the simulation for an unreconstructed $\text{Si}(111)$ surface with no arsenic overlayer (dashed line) by ≈ 0.29 atoms per row over the entire energy range studied. Since 1 atom per row corresponds to 3 ML for $[\bar{1}\bar{1}\bar{1}]$ channeling, 0.29 atoms per row is equivalent to 0.87 ML. The observation that 0.93 ML of As shadows 0.87 ML of underlying Si provides strong evidence for an epitaxial arsenic layer with high coherence.

Computer simulations were also performed for the surface peak measured along the $[\bar{1}\bar{1}\bar{1}]$ direction for the

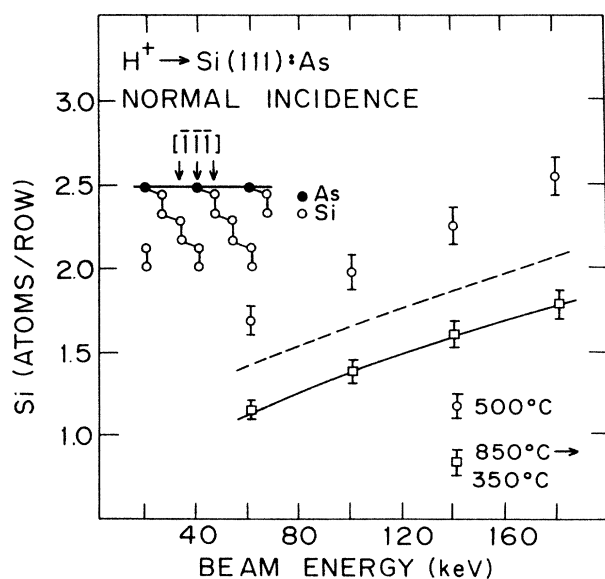


FIG. 1. Single alignment surface peak intensity as a function of incident proton energy for the $[\bar{1}\bar{1}\bar{1}]$ direction at 300 K. The full and broken curves are simulations for the $\text{Si}(111)\text{:As-}1\times 1$ surface and the $\text{Si}(111)\text{-}1\times 1$ surface, respectively. Data points for samples exposed to the As_4 molecular beam with different annealing conditions are shown: open circles are data for surfaces held at 500°C during the As_4 exposure (poor As epitaxy), and open squares are for surfaces cooled from 600 to 350°C during the As_4 exposure (good As epitaxy). In $[\bar{1}\bar{1}\bar{1}]$ 1 atom per row corresponds to 3 ML.

$\text{Si}(111)\text{:As-}1\times 1$ structure shown in Fig. 1. As input to the simulation, all silicon atoms were assumed to have a bulk vibration amplitude. The result of this simulation depends very weakly on the surface relaxation so that the surface vibration amplitude is the only unknown parameter to be adjusted. The results of the best-fit simulation are shown in Fig. 1 (solid line) for the best-fit arsenic one-dimensional vibration amplitude, $0.14 \pm 0.03 \text{ \AA}$. There is excellent agreement between the data points and the simulation.

As an example of a surface with what we consider to be poor As epitaxy, data are shown for a $\text{Si}(111)\text{:As}$ surface prepared at 500°C (open circles in Fig. 1). The Si yield is higher than the computer simulation for a bulk $\text{Si}(111)$ surface by between 0.83 and 1.45 ML. This surface exhibits a diffuse 1×1 LEED pattern with high background and the arsenic coverage is 0.94 ML. Also the surface adsorbed ≈ 1 ML of carbon and oxygen when exposed to air for 5 min. The higher Si yield and poor LEED pattern indicate that there are significant lateral displacements of surface atoms from bulk terminated positions. It has been pointed out by Patel⁸ that highly coherent epitaxy can not be obtained by exposing the $\text{Si}(111)$ surface to As_4 at a constant sample temperature, instead, it is necessary to cool the sample during the As_4 exposure, as described above.

Channeling and blocking directions for protons incident along the $[00\bar{1}]$ direction are shown in Fig. 2(a), and data for three different proton energies in the same geometry are shown in Figs. 2(b), 2(c), and 2(d) (solid curves). A clear shift of the blocking minima from bulk crystallographic directions [arrows in Figs. 2(b), 2(c), and 2(d)] towards higher scattering angles is observed and can be interpreted as an expansion of the surface interlayer spacing, D_{12} , with respect to the bulk Si interlayer spacing. Computer simulations were performed for which three parameters were varied: (1) the arsenic one-dimensional vibration amplitude, (2) the second layer silicon vibrational amplitude, and (3) the interlayer spacing between arsenic and silicon layers. The parameters that best fit the data were determined by an R -factor analysis with an R factor of the form

$$R = \frac{100}{N} \left[\sum_{i=1}^N \left(\frac{y^{\text{calc}} - y^{\text{expt}}}{y^{\text{expt}}} \right)^2 \right]^{1/2},$$

where y^{expt} is the measured yield and y^{calc} is the calculated yield for a set of N measured and calculated surface peak yields. A best-fit R factor of 0.59 was obtained over 234 data points for a silicon vibrational amplitude of $0.075 \pm 0.02 \text{ \AA}$ and an arsenic vibrational amplitude of $0.14 \pm 0.03 \text{ \AA}$ in agreement with the normal-incidence channeling results. The best-fit interlayer spacing D_{12} was $1.02 \pm 0.06 \text{ \AA}$ which is $30 \pm 8\%$ larger than the bulk interlayer spacing. Computer simulations using these values for the parameters are displayed in Figs. 2(b), 2(c), and 2(d) (broken curves). Satisfactory agreement between the experimental and calculated surface blocking curves is evident.

An outward relaxation of the $\text{Si}(111)\text{:As-}1\times 1$ surface has also been predicted by theoretical calculations: values for the expansion of 0.19 and 0.24 \AA have been reported

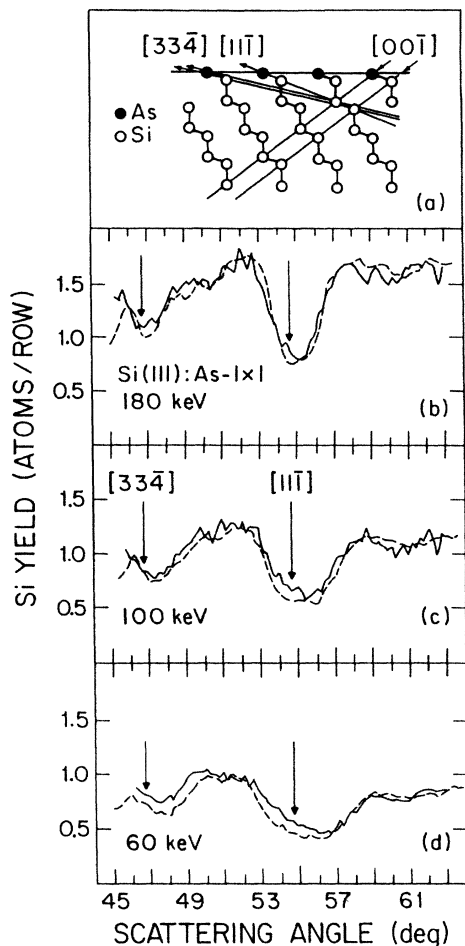


FIG. 2. (a) Channeling and blocking directions used to measure the surface relaxation of the well-ordered Si(111):As-1×1 surface. Surface blocking curves in $[00\bar{1}]$ channeling at three different beam energies: (b) 180 keV, (c) 100 keV, (d) 60 keV. The arrows denote the bulk blocking directions. Broken lines are Monte Carlo computer simulations of the Si(111):As-1×1 surface at the respective energies. For $[00\bar{1}]$ 1 atom per row corresponds to 2 ML.

(Refs. 2 and 9, respectively). Also, a recent x-ray standing-wave measurement of the surface expansion of 0.17 Å has been reported.⁸ All of these values are in reasonable agreement with the present result of 0.24 Å.

In order to demonstrate the uniqueness of this model, Fig. 3 shows computer simulations of the surface blocking curve for several different models in $[00\bar{1}]$ incidence at the most surface-structure sensitive proton energy of 60 keV. The broken curve in Fig. 3(a) is for a model with arsenic in a faulted site (the "faulted" structure has the surface stacking sequence . . . *aAbBa* instead of . . . *aAbBc*) with an arsenic one-dimensional vibrational amplitude of 0.14 Å and bulklike interlayer spacings. This is a plausible alternative to the model discussed above since 1 ML of As in a faulted site would passivate all surface dangling bonds without any inherent distortion of bond lengths or bond angles. The energy dependence of the simulated surface

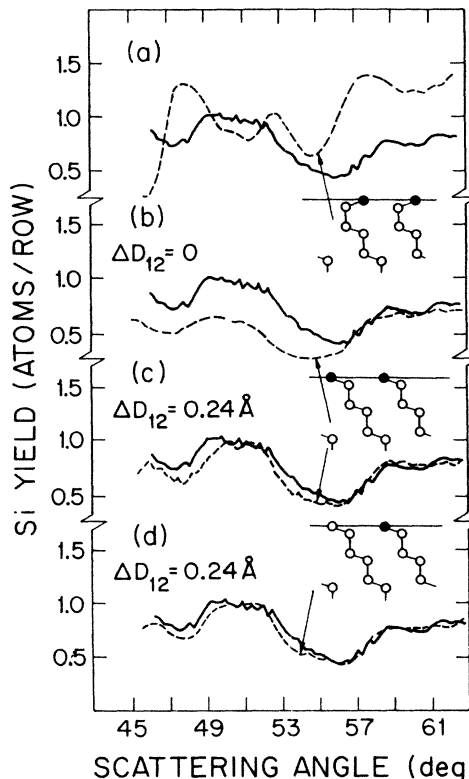


FIG. 3. Blocking curve in $[00\bar{1}]$ channeling at 60 keV. The data (solid lines) are reproduced four times with computer simulations for different surface structures (broken curves). Simulations are for (a) the As in a stacking-fault site, (b) a substitutional first-layer site with no surface relaxation, (c) a substitutional first-layer site with the best-fit relaxation, and (d) a model with the best-fit structure except that one out of every 14 surface atoms is Si, and the As one-dimensional vibrational amplitude is reduced to 0.13 Å.

peak in $[\bar{1}\bar{1}\bar{1}]$ incidence for this structure (not shown) agrees well with the data; however, it can be seen from Fig. 3(a) that the simulated blocking curve in $[00\bar{1}]$ incidence is in clear disagreement with the data. *This is compelling evidence that the arsenic layer does not occupy a stacking-fault site.* We have performed an *R*-factor analysis for models with only a small fraction of the surface As in the faulted site and the remaining fraction in the unfaulted site. The *R*-factor continuously increases from *R* = 0.59 at a faulted fraction of 0% to *R* = 1.0 at a faulted fraction of ≈ 20%. A complete discussion of this analysis will be included in a later publication.

The broken curve in Fig. 3(b) is for the model with As in a substitutional first layer site with no relaxation of the surface layer ($\Delta D_{12} = 0$). A comparison of this curve with the data shows that there is a much larger discrepancy than was found for the best-fit model [Fig. 2(d)] which is reproduced in Fig. 3(c). In particular, the position of the blocking minima in Fig. 3(b) lie at lower scattering angles than the minima of the data.

The As coverage measurement of 0.93 ML indicates that a small fraction of the surface may have other surface

structures with <1 ML As coverage. We have performed computer simulations for a number of structures affecting from 7% to 14% of the surface that give acceptable agreement with the data. As an example, Fig. 3(d) shows a simulated surface blocking curve in $[00\bar{1}]$ incidence for a model with the best-fit structure and relaxation described above, except that only 93% of the surface Si atoms have been replaced by As, and the As vibrational amplitude has been reduced to 0.13 \AA . No surface or sub-surface distortions due to the lower symmetry of the surface have been included in the model. The fit is comparable to the fit for the perfect 1×1 surface, and the total R factor over the three energies studied is 0.51 which is actually lower than the R factor obtained for the best-fit perfect 1×1 surface ($R=0.59$). *Therefore, it is possible to improve the agreement with the data by introducing an arsenic deficiency of the surface into the ideal 1×1 structure.* We note that including other surface structures and subsequent strain-induced distortions of the surface lead to best-fit As vibrational amplitudes that are, in general, smaller than 0.14 \AA .

In conclusion, we have measured the surface peak intensity in the $[\bar{1}\bar{1}\bar{1}]$ direction and surface blocking curves near the $[11\bar{1}]$ direction for the Si(111):As- 1×1 surface.

The energy dependence of the $[\bar{1}\bar{1}\bar{1}]$ surface peak is well below the level expected for a bulk terminated Si(111)- 1×1 surface, indicating a high degree of arsenic epitaxy. The surface blocking curves near the $[11\bar{1}]$ direction are shifted towards a higher scattering angle indicating an outward relaxation of the As layer from the bulk position. Comparison of the surface blocking curves with Monte Carlo simulations shows that $D_{12}=1.02 \pm 0.06 \text{ \AA}$ and the As vibration amplitude is $0.14 \pm 0.02 \text{ \AA}$. An analysis of possible defect structures shows that approximately 7%–14% of the surface may deviate from this ideal structure.

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