In/Si(111)-$\sqrt{3}\times\sqrt{3}$ Interface: An Unrelaxed T_4 Geometry

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Back reflection x-ray standing waves and surface extended x-ray absorption fine structure have determined the atomic coordinates (i.e., the perpendicular displacement *and* the near-neighbor bond lengths) at the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ interface. Although the In adatoms are found to reside at a single position, 2.10 ± 0.06 Å above the first Si bilayer, dual In-Si near-neighbor distances are found: 2.73 ± 0.02 Å to the first- and 2.49 ± 0.03 Å to the second-layer Si atoms, respectively. Contrary to the accepted model, our data suggest that the T_4 geometry is not relaxed.

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Although the structural aspects of semiconductor interfaces have become better understood over the past two decades, a complete description of the atomic coordinates for a given structure has been postulated for only a handful of model systems. In many cases, these coordinates arise from either sophisticated theoretical calculations, for which there exists no complete experimental counterpart with which to evaluate them, or elastic low energy electron diffraction (ELEED), a technique which is model dependent and requires nearly as much computation as a complete first principles approach.

In 1964, Lander and Morrison discovered that the adsorption of the column-III metals Al and In induced a $\sqrt{3}\times\sqrt{3}R30°$ reconstruction on the (111) face of Si [1]. Because of the trivalency of the metals, they concluded that for 1/3 monolayer (ML) coverage, the metal atoms would occupy the threefold hollow sites, termed H_3, above three first-layer Si atoms. This assignment was based on the high symmetry of the geometry and the saturation of the substrate dangling bonds, which result in a lower total energy.

In 1984, Northrup performed first-principles pseudopotential total-energy and force calculations for the first of this class of structures [2]. He found that when Al was placed on the ideal Si(111) surface, the H_3 geometry was in fact an energy minimum. However, using the Hellman-Feynman theorem, he found that another geometry, the T_4, which places the metal atom on the adjacent threefold eclipsed site directly above a second-layer Si atom, is the more energetically favored when substantial ($\sim$0.3 Å) substrate relaxation is allowed.

This discovery was startling, for in this geometry the metal atoms each have four Si neighbors, three in the surface layer and one in the second layer directly below. The T_4 site therefore has several unique properties over those of the H_3. These include four versus three Si neighbors to the adatom, a large difference in the perpendicular height of the adatom due to its interaction with the second-layer Si atom, and, perhaps most significantly, substantial energy-favored substrate relaxation.

Because of the prototypical nature of these interfaces (which lends itself to calculation), the general lack of precise structural data is surprising, and Northrup's calculations, performed nearly a decade ago, still stand as the state of the art. In fact, the general body of knowledge related to substrate relaxation is scant; it is typically assumed in the analysis of structural data that the substrate surface atoms, although initially reconstructed, revert to their ideal bulklike geometry in the presence of the adsorbate.

Although the T_4 site is no longer questioned as the energy minimum for any of the group-III metals [2–5], an exact experimental determination of its atomic coordinates would substantially further the field of surface physics, for it is now recognized that the T_4 site is the most common building block for all the (111) faces of the technologically relevant metal-semiconductor interfaces in addition to the clean surfaces themselves [6].

In this work, we combine two independent structural probes: back-reflection x-ray standing waves (BRXSW), which accurately measures perpendicular distance, and surface extended x-ray absorption fine structure (SEXAFS), which accurately measures near-neighbor bond lengths, to obtain a full microscopic structural determination of the 1/3 monolayer In/Si(111)-$\sqrt{3}\times\sqrt{3}$ interface. Because we determine both the perpendicular distance of the adatom to the bulk diffracting planes and the bond lengths of the adatom to the near-surface substrate atoms, our structural determination includes the degree of substrate relaxation [7], a critical yet experimentally overlooked interfacial parameter. In light of our findings, this system may now be used to test new computational schemes and also the complex theoretical potentials used in ELEED analysis.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory in a standard ultrahigh vacuum chamber equipped with a double pass cylindrical mirror analyzer (CMA). Clean Si(111) 7×7 surfaces were prepared by flashing degreased and degassed Si(111) wafers to temperatures exceeding 1000 °C. The In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surfaces were prepared by depositing approximately 1/3 monolayers of In from a thoroughly degassed W coil followed by heat treatment between 450° and 575 °C [4,5]. An excess In would contribute In-In backscattering to the SEXAFS signal and therefore interfere with the determination of the In-Si bond lengths, care was taken not to overshoot the 1/3 ML coverage for the SEXAFS portion of the experiment. For the XSW experiment, additional In is not as large a concern, for it would add only an incoherent contribution to the yield which is readily detected.

BRXSW data were collected in a fixed-angle normal-incidence diffraction geometry by scanning a pair of InSb(111) monochromator crystals through the Si(111) Bragg back-reflection condition, which occurs near 1977 eV. In a single BRXSW scan, the back-reflected photon intensity and the In *MNN* (∼400 eV) Auger yield are measured as functions of photon energy around the Bragg condition. Similar data are recorded with the CMA kinetic energy set above the In Auger line. Subtracting the background signal from the signal at the Auger peak leaves the absorption profile, *Y*, of the overlayer in the field of the standing wave. The reflectivity spectra *R* were measured by the incident flux monitor upstream of the sample; it consisted of an 80% transmitting Ni grid and a channeltron. As the energy is swept through the Bragg condition, the back-reflected beam intensity from the crystal at normal incidence is observed on top of the signal from the incident flux. The detection of the reflectivity peak is critical for the analysis because it provides fiducial information on the energy resolution and energy calibration as well as control of the sample alignment.

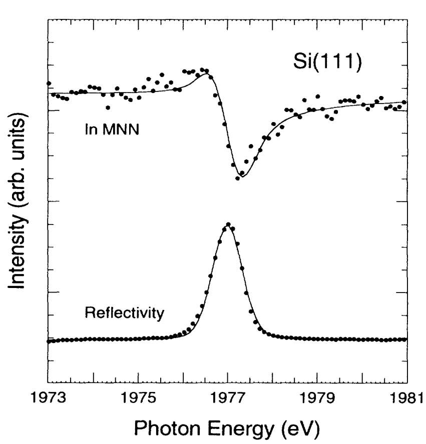

FIG. 1. Photon-energy dependence of the reflectivity and the background corrected In *MNN* x-ray standing wave near the Si(111) Bragg back-reflection condition for the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface. The solid lines are the best fits to the data points (see text).

Figure 1 shows the Si(111) reflectivity along with the best fit to the data points [8]. The fit is the result of convolving the theoretical reflectivity with a Gaussian of width 0.70 eV and adjusting it for a small energy offset. Also shown is the In standing wave pattern compared to its best fit to the function

$$Y=1+R+2\sqrt{R}F\cos(\phi-2\pi\nu)\,,$$

using the energy offset and Gaussian width obtained from the fit to the reflectivity. The pertinent fitting parameters here are ν, the adsorbate substrate distance in units of the reflecting plane spacing, and F, the coherent fraction of atoms at ν. These values are determined to be 0.67 $\pm$0.02 and 0.93$\pm$0.08, respectively, which locate the In atoms 2.10$\pm$0.06 Å above the middle of the Si(111) extrapolated surface bilayer with a fractional occupancy close to 1, i.e., single site adsorption. This relatively high coherent fraction indicates that any additional In beyond 1/3 ML was desorbed by the higher annealing temperatures.

Figure 2 shows the top and side views of the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ T_4 geometry. Here, the In adatoms reside in the Si(111) threefold eclipsed sites directly above a second-layer Si atom. The size of the In and Si atoms have been scaled to their covalent radii [9]. As the standing wave data determine only the position of the In atoms relative to the extrapolated bulk planes, we have placed the In atom at a location above the bilayer which assumes *a priori* that there is no subsurface relaxation (i.e., the topmost Si atoms are in their ideal bulk-terminated geometry); this assumption is evaluated below. Since the distance between the two Si layers of the bilayer is 0.784 Å, this places the In atoms 1.71$\pm$0.06 Å above the first-layer Si plane and 2.49$\pm$0.06 Å directly above the second-layer Si atom. Because we know the Si-Si distance within the first layer of this hypothetical structure (3.84 Å), we may also calculate the resulting In-Si bond lengths; they are 2.80$\pm$0.06 Å to the first- and

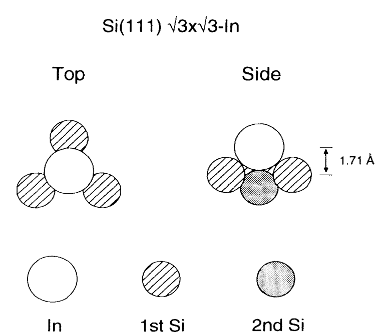

FIG. 2. Top and side views of the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ T_4 geometry deduced from this work. The relative sizes of the In and Si atoms have been scaled to their covalent radii.

2.49 ± 0.06 Å to the second-layer Si atoms, respectively. For comparison, the sum of the In and Si covalent radii is 2.55 Å.

In order to *experimentally* determine the bond lengths within this structure, the top half of Fig. 3 shows the raw $k^2\chi(k)$ In L_3 SEXAFS data from the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface together with its first-shell Fourier-filtered contribution. These data were recorded at the "magic" angle, 54.7° from glancing incidence [10], in the constant final state mode (CFS) [11] by scanning a pair of Ge(111) monochromator crystals through the In L_3 absorption edge, which occurs near 3730 eV, and monitoring the intensity of the In *MNN* Auger yield as a function of photon energy and flux. The bottom half of the figure shows similar bulk-sensitive total-yield data from crystalline InP, which has known structure. Because P differs by only 1 in atomic number from Si, InP is an excellent phase and amplitude standard with known crystallography with which to analyze the In-Si bond.

Immediately evident from the raw SEXAFS data is that the first-neighbor bond length, which is proportional to the lowest frequency of the EXAFS oscillations, is significantly larger, by ~ 0.2 Å, at the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface than in crystalline InP with a first-neighbor distance of 2.54 Å. Since the sum of the In and Si covalent radii is 2.55 Å, the primary distance at the surface is, surprisingly, much larger than this expected sum [12]; therefore, more quantitative analysis is needed to understand the exact nature of this bonding.

Following standard EXAFS procedures [13], first-shell phase, $\phi(k)$, and amplitude, $|f(k)|$, functions were extracted from the bulk InP standard. The upper half of Fig. 4 compares the Fourier-filtered first-shell SEXAFS data for the In-Si bond length to its least squares fit to the function $k^2\chi(k)$, where

$$\chi(k) = N|f(k)|\sin[2kr + \phi(k)] .$$

In the fit, only the linear parameter N, the In-Si coordination number, and the nonlinear parameter r, the In-Si bond length, were varied. The best fit was obtained with $N = 1.8 \pm 0.4$ and $r = 2.67 \pm 0.04$ Å. It is clear, however, that this fit does not accurately represent the data, for it is well outside the experimental error bars, which can be estimated from the statistical noise in the raw $k^2\chi(k)$, for both high and low values of k. Furthermore, the T_4 (or H_3) geometry, has four (or three) Si near neighbors to the adatom, not approximately two as the fit has determined.

To better model the SEXAFS data, the lower half of Fig. 4 shows a two component fit to the same data assuming dual near-neighbor bond lengths as suggested by the independent x-ray standing wave experiment and by Northrup's calculations. Clearly, this fit does represent the data; the residual χ^2 is reduced by more than a factor of 10 over the previous single-bond length model. The values determined here are 2.7 ± 0.4 Si atoms at 2.73 ± 0.02 Å and 1.3 ± 0.4 Si atoms at 2.49 ± 0.03 Å. These bond lengths are nearly identical (within the experimental error) to those calculated from the results of the BRXSW measurement under the *a priori* assumption of negligible distortion of the T_4 site. Additionally, the coordination numbers are equivalent to three first-layer Si atoms and one second-layer one, confirming the location of the adatom as depicted in Fig. 2.

Because the XSW technique determines only the adatom distance relative to the bulk diffracting planes, information on surface relaxation, distortion, and bond lengths is not obtained from a BRXSW experiment. However, because we have independently measured the adatom-

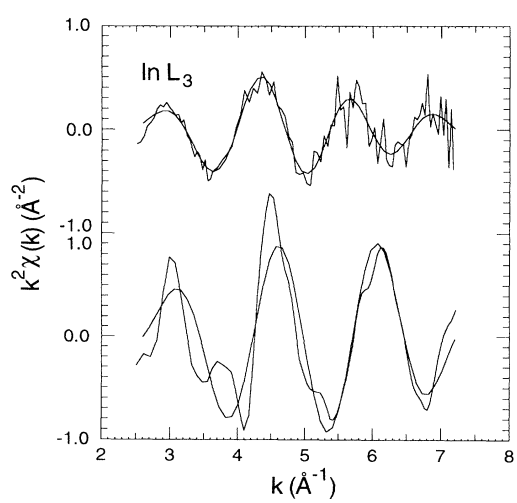

FIG. 3. Raw In $L_3k^2\chi(k)$ EXAFS data from the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface (top) and from crystalline InP (bottom) plotted with their first-shell Fourier-filtered contributions.

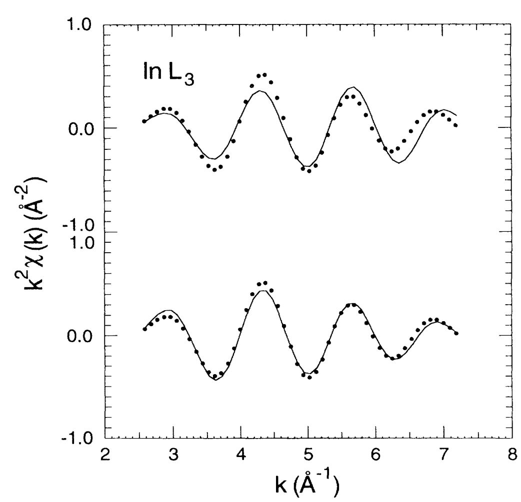

FIG. 4. Fits to the first-shell EXAFS data from the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface assuming one (top) and two (bottom) first-neighbor bond lengths. The solid lines are the fits, and the dots are the data points of the backtransforms.

substrate near-neighbor bond lengths from SEXAFS, and the BRXSW and SEXAFS determinations so closely coincide, we can conclude that the degree of subsurface distortion at this interface is much smaller than theoretically predicted. Had the amount of distortion established by Northrup's calculations been present, a discrepancy of ~0.3 Å between the two experiments (in particular, the location of the second layer Si atom beneath the adatom) and the ideal unrelaxed interface would exist. Moreover, Northrup finds In-Si bond lengths of 2.63 Å to the first- and 2.59 Å to the second-layer Si atoms. The difference between these lengths is only 0.04 Å, which is much smaller than the experimental value of 0.24±0.05 Å. An earlier XSW study found a similar discrepancy of 0.16 Å between the experimental and calculated Ga position on the Ga/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface [14].

It is interesting to compare the experimental SEXAFS bond lengths to the bond lengths within the corresponding crystalline structures. In InP, a tetrahedrally bonded covalent material, the bond length is 2.54 Å. Because Si is only one less in atomic number than P, it would have been expected that the In-Si length be close to this value. However, in its natural form, In is a tetragonal metal which possesses twelve first neighbors. The closer eight of these neighbors are at a distance of 3.20 Å [15]. The sum of this metallic radius with the covalent radius of Si is then 2.71 Å, nearly identical to the SEXAFS determination of the In-first-layer Si bond length. Astonishingly, it is the In-second-layer Si distance which corresponds to the sum of covalent radii; apparently, this is the closest the In adatom can come to the substrate. We may speculate that the In-Si bonds to the first layer are much longer than their covalent sum since their deviation from tetrahedral geometry is so great (the original Si dangling bonds point normal to the surface). As a counterexample, the Sb-Si bond length at the Sb/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface is the same as in crystalline AlSb, 2.66±0.03 Å [16]. In this case, the Sb atoms sit atop the first-layer Si atoms, rather than bridging them.

It is instructive to question why Northrup's calculations overestimate the amount of subsurface distortion to such an extent. To first order, the change in height of the second-layer Si atom (Δz_2) directly beneath the adatom is given by the inward displacement of the first-layer Si atoms (Δr_1) towards the adatom: $\Delta z_2 = 2\sqrt{2}\Delta r_1$. Therefore, even a relatively small error in bond length (~0.1 Å) will produce a relatively large error (~0.3 Å) in the degree of substrate relaxation. It is this structural interplay which accounts for the discrepancy between the previously accepted model and experiment.

In conclusion, through a novel combination of BRXSW and SEXAFS, we have performed a microscopic determination of the geometric structure of the In/Si(111)-$\sqrt{3}\times\sqrt{3}$ interface which includes the degree of substrate relaxation. Although our data support the T_4 location for the group-III metal Si(111) interfaces, our structural findings contradict the popular belief that the stability of this geometry originates from substrate relaxation. It is our hope that this experiment will encourage future effort to improve the initial approximations of *ab initio* calculation and the ability of theory to more accurately predict bond lengths at surfaces and interfaces.

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