

Arsenic overlayer on Si(111): Removal of surface reconstruction

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The complex reconstruction characteristic of annealed Si(111) surfaces is removed by the interaction of As with the clean Si(111) 7×7 surface. Surface-sensitive core-level spectroscopy measurements of the Si(111):As 1×1 surface reveal a well-ordered surface with threefold-coordinated As atoms replacing the Si atoms in the outermost layer. The absence of dangling bonds in this structure leads to an unreconstructed surface which is highly resistant to contamination.

While many factors such as strain¹ and correlation energies combine with the electronic energy to determine the microscopic structure of a reconstructed surface such as Si(111) 7×7 ,² the high energy of the ideal Si(111) surface arises from the existence of metallic dangling-bond orbitals. If these orbitals could be either removed or filled, the driving force for reconstruction would be removed, and a 1×1 surface should result. We find that this situation is realized in practice by arsenic termination of the Si(111) surface. The atoms in bulk Si are tetrahedrally coordinated with sp^3 hybridized bonding orbitals. At the (111) surface, Si atoms in the top layer have only three bonds, leading to instability and reconstruction. Arsenic, on the other hand, prefers a threefold coordination, with three orbitals taking part in bonding and the two remaining valence electrons in a nonbonding "lone-pair" state. If As atoms substitute for the surface Si atoms at the (111) surface, all atoms can be optimally bonded (see Fig. 1). Each Si atom in the bulk (b) is bonded to four Si atoms; each interface Si atom (a) is bonded to one Si and three As atoms; each As atom at the surface (shaded in Fig. 1) is bonded to three Si atoms. The result is an unreconstructed, stable Si(111):As 1×1 surface.

This configuration is similar to the situation of As on Ge(111) which has been studied with angle-resolved photoemission spectroscopy.³ However, in the germanium case the As atom is nearly the same size as the Ge atom it is replacing, so that terminating the surface with As does

not lead to a large strain at the surface. For the silicon surface, the possibility exists that the larger As atom will lead to a strain-induced reconstruction. This does not happen, indicating that dangling-bond removal dominates over strain effects. It should be noted that As termination of the Si(111) surface is quite different from the 1×1 surface structure which results from chlorine adsorption⁴ on Si(111) 2×1 or hydrogen adsorption⁵ on Si(111) 2×1 and Si(111) 7×7 . In the case of Cl or H termination, the monovalent adatom passivates the surface by capping a single silicon dangling bond; in the case of As termination, we will show that the arsenic replaces the top silicon layer, bonding to three silicon atoms and terminating the surface with a nonreactive lone-pair orbital. We expect that the As atoms relax outwards from the bulk Si lattice sites, as has been discussed³ for Ge(111):As 1×1 .

In contrast to the Si(111):As 1×1 surface, the ideal, bulk-terminated, Si(111) surface would contain a single half-filled "dangling-bond" orbital on each surface atom. This ideal surface is not stable, and the Si(111) surface reconstructs to eliminate these half-filled orbitals. On the cleaved surface, the 2×1 reconstruction is widely believed to involve formation of π -bonded chains of atoms in a structure which contains no partially filled orbitals.⁶ The annealed Si(111) 7×7 reconstruction is a more complex structure, including a combination of dimers, adatoms, and stacking faults, as discussed by Takayanagi, Tanishiro, Takahashi, and Takahashi.⁷ These features of the surface reconstruction would lead to defects in epitaxially grown layers if the reconstruction were not healed during interface formation. An understanding of both the origin of the surface reconstruction and its behavior during chemisorption is therefore essential to the study of heteroepitaxy.⁸ This investigation of the Si(111):As surface contributes to an understanding of both the mechanisms which lead to surface reconstruction and the physics of GaAs epitaxy on Si substrates.

We have studied the interaction of As with the Si(111) 7×7 surface using surface-sensitive core-level spectroscopy. Since different bonding configurations result in different core-level binding energies, the Si and As core levels can be utilized as a critical test of the model discussed above for Si(111):As 1×1 . The Si(111) 7×7 surface contains a large number of inequivalent sites, leading to many components in the Si core-level spectra. Upon As expo-

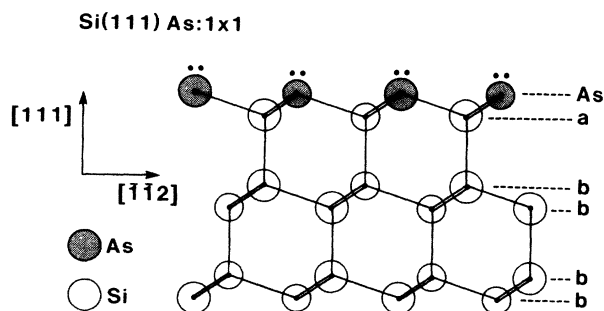


FIG. 1. Side view in the $(\bar{1}10)$ plane of the Si(111):As 1×1 surface. The As atoms substitute for the top Si layer, resulting in a stable, unreconstructed surface.

sure, we find the broad Si $2p$ core-level spectrum characteristic of the 7×7 reconstruction to be replaced by two distinct components. These components are identified with bulk and interface Si atoms, denoted (b) and (a), respectively, in Fig. 1. The As $3d$ core level, as expected in this substitutional model, exhibits only a single component, and low-energy electron diffraction (LEED) exhibits a sharp 1×1 pattern for the Si(111):As surface.

The Si(111):As 1×1 surface is also extremely stable with respect to either thermal annealing or contamination. The As is more strongly bound to the Si(111) surface than it is to either GaAs or solid As, requiring anneals at $> 700^\circ\text{C}$ to remove As from the surface. The absence of unsaturated bonding orbitals on the Si(111):As surface greatly reduces the susceptibility of the surface to adsorption of either additional As or contaminants such as oxygen.

In the performance of these experiments, clean Si(111) 7×7 substrates were exposed to arsenic using an As_4 molecular beam. Unless otherwise noted, the p -type (boron, $\sim 10\ \Omega\text{cm}$) Si substrates were held at 350°C during the deposition by running a direct current through them. The cleanliness of the sputtered (500-eV Ar^+ ions) and annealed ($\sim 850^\circ\text{C}$) Si(111) 7×7 surfaces was established using both Auger electron spectroscopy and the Si $2p$ core-level spectrum. The photoemission measurements were performed at the Stanford Synchrotron Radiation Laboratory (beamline I-1) using photon energies in the range $70\text{--}130\ \text{eV}$. The photoelectrons were collected by a double-pass cylindrical mirror analyzer with the sample normal at an angle of 3.5° from the analyzer axis. With the experimental parameters used, the Fermi edge of a clean gold film was found to have a full width of $0.26\ \text{eV}$ for $\hbar\omega = 130\ \text{eV}$.

When the clean Si(111) 7×7 surface held at $\sim 350^\circ\text{C}$ is exposed to arsenic, the low-energy electron diffraction pattern converts to a sharp 1×1 structure. The effect of the reordering of the Si(111) 7×7 surface upon interaction with arsenic can be seen in Fig. 2. The figure depicts the Si $2p$ core level for the clean [Fig. 2(a)] and arsenic covered [Fig. 2(b)] surfaces. Both bulk sensitive ($\hbar\omega = 108\ \text{eV}$, electron kinetic energy $\sim 3\ \text{eV}$) and surface sensitive ($\hbar\omega = 130\ \text{eV}$, electron kinetic energy $\sim 25\ \text{eV}$) spectra for the clean Si(111) 7×7 surface are shown in the lower panel. The bulk sensitive spectrum is dominated by a single spin-orbit pair characteristic of bulk silicon. This spectrum establishes the location of the Si $2p_{3/2}$ bulk component relative to the Fermi level on the clean Si(111) 7×7 surface.

The surface-sensitive spectrum ($\hbar\omega = 130\ \text{eV}$) in Fig. 2 for Si(111) 7×7 indicates the presence of surface components shifted to both higher and lower binding energies from the bulk peak. A unique deconvolution of the spectrum into the bulk and various surface components is not possible. The line shape is indicative of a number of components which are separated by less than the experimental resolution. This is expected due to the large number of inequivalent sites on the Si(111) 7×7 surface: adatoms, dimer atoms, dangling-bond atoms, etc.

In strong contrast to the Si(111) 7×7 results, the Si $2p$ spectrum for the Si(111):As 1×1 surface [Fig. 2(b)] ex-

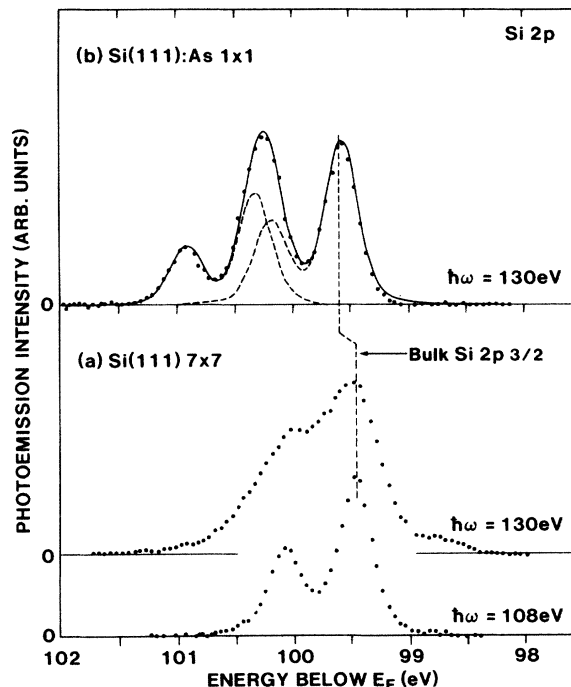


FIG. 2. (a) Bulk sensitive ($\hbar\omega = 108\ \text{eV}$) and surface sensitive ($\hbar\omega = 130\ \text{eV}$) Si $2p$ spectra for the clean Si(111) 7×7 surface. (b) Surface sensitive Si $2p$ spectrum for the Si(111):As surface. The solid line is the sum of the interface and bulk components (dashed lines) with fitting parameters listed in the text. The spectrum intensities have been arbitrarily scaled with respect to one another after the subtraction of a quadratic background.

hibits only two spin-orbit pairs: one arising from bulk silicon atoms, and an interface component shifted by $0.75 \pm 0.01\ \text{eV}$ to higher binding energy. The solid line in the figure is the result of a least-squares fit to the data of two spin-orbit pairs of equal width [spin-orbit splitting equal to $0.600\ \text{eV}$; $2p_{3/2}$ to $2p_{1/2}$ intensity ratio equal to statistical value of 2:1; Lorentzian full width at half maximum (FWHM) equal to $0.075\ \text{eV}$; Gaussian broadening FWHM equal to $0.30\ \text{eV}$]. These results confirm that the sharp 1×1 LEED pattern is the result of an ordered surface. The two components in the core-level spectrum can be associated with the atoms marked (a) and (b) in Fig. 1. The atoms in a bulklike configuration (b) give rise to $\sim 60\%$ of the Si $2p$ emission. The silicon atoms (a) which have three bonds to the more electronegative As give rise to the component which is shifted to higher binding energy. The measured interface-to-bulk intensity ratio of 0.68 is consistent with an electron escape depth (kinetic energy $\approx 25\ \text{eV}$) of $\sim 4\ \text{\AA}$, assuming the model in Fig. 1. The shift in position of the bulk Si $2p_{3/2}$ component between the clean and As-covered surfaces seen in Fig. 2 arises from a difference in band bending of $0.13\ \text{eV}$ between the two surfaces. This difference in band bending varied with the surface condition between 0.10 and $0.34\ \text{eV}$, as discussed below. The spectrum in Fig. 2(b) was obtained after a 2-min, 300°C anneal of the Si(111):As surface.

The Si $2p$ core-level data discussed above show that

there is only one interface Si site on the Si(111):As 1×1 surface. The existence of a single site for the As atoms is suggested by the As $3d$ core-level spectra in Fig. 3. The As $3d$ spectrum always consisted of a single spin-orbit pair with an As $3d_{5/2}$ binding energy 58.17 ± 0.01 eV less than that of the Si $2p_{3/2}$ bulk component. The solid line through each spectrum in Fig. 3 is a least-squares fit to spectrum 3(b) [taken simultaneously with spectrum 2(b)] with a spin-orbit splitting of 0.691 eV and the statistical intensity ratio of 3:2. The As $3d$ spin-orbit pair has a fitted Lorentzian linewidth (FWHM) of 0.16 eV, convoluted with a Gaussian broadening (FWHM) of 0.38 eV. The As $3d$ core level in Fig. 3 is shown for four cases: (a) 44 h after the initial 10-sec exposure of Si(111) 7×7 to As₄ at a substrate temperature of 350°C, (b) after a 2-min, 300°C anneal, and after extended further exposures [(c) 10 sec [$\sim 10^4$ L (where 1 L = 10^{-6} Torrsec)] and (d) 300 sec ($\sim 3 \times 10^5$ L)] of the room temperature Si(111):As 1×1 surface to the As₄ molecular beam. The four spectra, which have been aligned with respect to the bulk Si $2p_{3/2}$ peak and normalized to constant area, can be seen to be essentially identical. Similar results were found for the Si $2p$ spectra. The ratio of the area under the As $3d$ peak to that of the Si $2p$ emission was constant ($\pm 1.4\%$) for spectra 3(a)–3(c). A small increase ($\sim 13\%$) in the As $3d$:Si $2p$ area ratio was seen following the 3×10^5 L exposure to

As₄ [Fig. 3(d)]. It should be pointed out that a thick film of amorphous arsenic can be grown on the Si(111):As surface if As₂ molecules are used instead of As₄, and if the exposure is carried out on a room-temperature substrate. Our data for these thick films show that there is no detectable chemical shift between As in the site shown in Fig. 1 and in the thick As film. The excess arsenic is bound to the surface only weakly, however, and can be removed by annealing at 200°C. This is in contrast to the $> 700^\circ\text{C}$ anneal required to remove the monolayer of As bonded to the substrate.

The separation (0.75 ± 0.01 eV) and intensity (0.68 ± 0.01) of the surface-shifted Si $2p$ peak relative to the bulk component, as well as the line shape of the As $3d$ core level and the separation between the bulk Si $2p_{3/2}$ and As $3d_{5/2}$ peaks (58.17 ± 0.01 eV), were found to be constant throughout the entire range of experimental conditions for $\hbar\omega = 130$ eV. The Gaussian component of the linewidth (FWHM) for the Si $2p$ peak was found to be 0.32 ± 0.02 eV, with the Lorentzian component (determined by lifetime effects) held constant (FWHM = 0.075 eV) during the fitting procedure. The constancy of the various fitting parameters implies that no arsenic is removed from the surface during a 300°C anneal, nor added to the surface during $\sim 10^4$ L room-temperature exposure to As₄. Areas of the surface which are not covered with a monolayer of As should give rise to additional components in the Si $2p$ spectrum. It is possible to force a third component into the fit, but it can never make up more than (5–8)% of the total, and its position is not consistent among the various spectra. As discussed above, adsorption of additional As atoms beyond monolayer coverage would not be evident as a second component in the As $3d$ spectrum. The small increase in the As:Si area ratio after the room temperature exposure to $\sim 3 \times 10^5$ L of As₄ (not accompanied by significant changes in the other parameters) indicates approximately 10% of a monolayer of excess arsenic in this case of extended exposure.

The position of the spectra with respect to the Fermi level varies as a function of time. Immediately following deposition, the bulk Si $2p_{3/2}$ peak is at a binding energy 0.10 eV greater than that of the clean Si(111) 7×7 surface. Over a period of hours in the UHV chamber, the Fermi level shifts ~ 200 meV closer to the conduction band. This may be due to adsorption of additional As from the background As₄ pressure in the UHV chamber, as a 300°C anneal returns the Fermi level to close to its original position. We estimate that only $\sim 10^{-4}$ of a monolayer is necessary for this change in the Fermi level. Further exposure to As₄ of the room-temperature substrate likewise raises the Fermi level in the gap. Taking the clean Si(111) 7×7 surface Fermi level to be 0.6 eV from the valence-band maximum⁹ implies that the Fermi level on the Si(111):As surface varies between 0.7 and 0.9 eV from the valence band of the *p*-type silicon.

The stability of the surface against adsorption of additional As₄ is due to the absence of dangling bonds on the As atoms. The Si(111):As surface is also resistant to the chemisorption of residual gases in the UHV chamber. In particular, we find the As-terminated surface to be a factor of $\sim 10^7$ less sensitive to oxygen chemisorption than

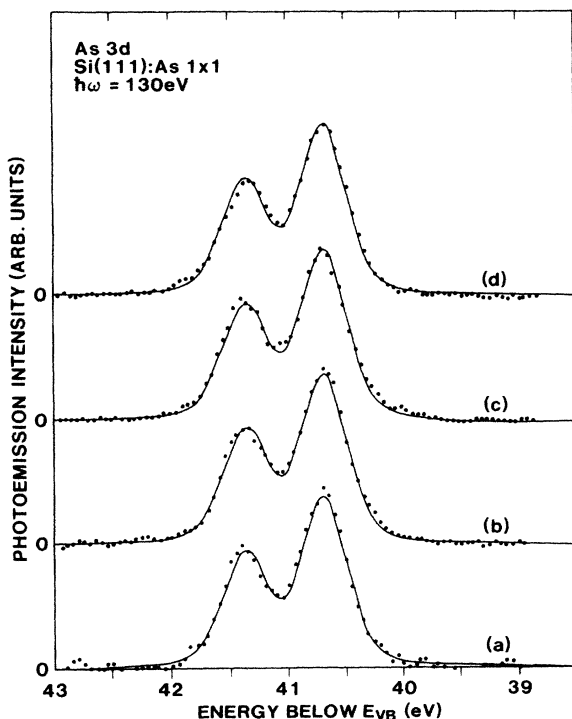


FIG. 3. As $3d$ core-level spectra at $\hbar\omega = 130$ eV. The solid line through each spectrum is a fit to spectrum (b) (see text). (a) 44 h post deposition; (b) after 2-min, 300°C anneal; (c) the initial $\sim 10^4$ -L exposure (10 sec in As₄ beam) was repeated with the sample at room temperature; (d) after $> 10^5$ L (300 sec in As₄ beam) room-temperature arsenic exposure. A linear background has been subtracted from the data.

the clean Si(111) 7×7 surface. The full coordination of the arsenic-terminated surface (see Fig. 1) means that additional atoms must break Si—As bonds in order to chemisorb to the surface. The Si—As bond is very strong, however, as is evidenced by the $> 700^\circ\text{C}$ thermal desorption temperature for As on the Si(111):As 1×1 surface, making such a reaction unlikely.

The combination of (i) the 1×1 LEED pattern, (ii) the core-level deconvolution results showing only one Si interface site and one As site, and (iii) the extreme resistance of the surface to contamination and additional As adsorption provides very strong evidence for the model of the Si(111):As 1×1 surface shown in Fig. 1. Total energy calculations for this model,¹⁰ show that the minimum energy occurs for a separation of 0.97 Å between the As layer and the outermost Si layer (placing the As layer 0.19 Å outside the bulk Si lattice sites). Although a model in which the As atoms occupy the on-top site of the ideal Si(111) surface would be consistent with (i) and (ii), this structure would contain two half-filled As dangling bonds in addition to the lone pair and would certainly not be stable against contamination. The core-level results and the sharp 1×1 LEED pattern also show that the Si(111):As surface is well ordered. A strong disordering of the surface would lead to a greater number of chemically shifted core-level components for both Si and As than are observed. A large degree of order is also required to explain

the strong surface state dispersion which we observe in angle-resolved photoemission¹⁰ for Si(111):As 1×1 .

In summary, we find that the strong reconstruction of the Si(111) 7×7 surface is removed upon exposure to As. All of our results support a model structure for the Si(111):As 1×1 surface where a monolayer of As atoms replaces the outermost Si layer of a bulk-terminated (111) surface. This leads to a stable, 1×1 structure in which all atoms are optimally coordinated and there are no partially filled orbitals. The chemical energy gained by terminating with As allows the considerable atomic rearrangement necessary from the Si(111) 7×7 geometry and shows that this reconstruction can be removed at relatively low temperatures. The passivated, unreconstructed surface is important for an understanding of the initial stages of GaAs heteroepitaxy on Si. In particular, the stability of the As-terminated surface strongly suggests that the first stage for GaAs growth, in which Ga is evaporated in the presence of an As_4 flux, will be the structure shown in Fig. 1.

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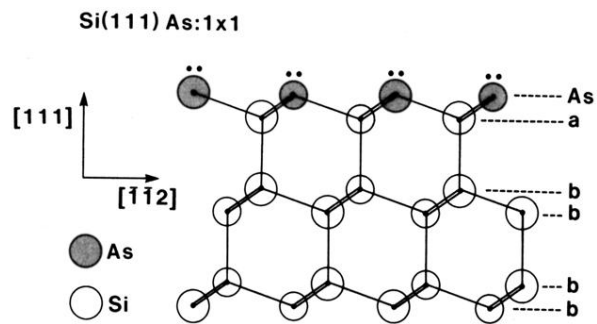


FIG. 1. Side view in the $(\bar{1}10)$ plane of the Si(111):As 1×1 surface. The As atoms substitute for the top Si layer, resulting in a stable, unreconstructed surface.