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In-plane structure of arsenic deposited on the Si(111) surface studied with the grazing-angle x-ray standing-wave method

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The in-plane structure of the Si(111):As-1×1 surface has been studied under ultrahigh vacuum using x-ray standing waves produced by a substrate silicon crystal in the grazing-angle diffraction geometry. The observed As fluorescence profiles are consistent with models indicating a bulklike surface with threefold-coordinated As atoms in the first layer. Evidence indicating that the As atoms occupy these high-symmetry sites with little disorder is obtained from investigation of the dependence of fluorescence profiles on the displacement and order parameters.

The x-ray standing-wave (XSW) method[1,2] is one of the few methods that can provide model-independent information on the lattice position of foreign atoms at surfaces and interfaces in real space. XSW's formed by the interference of the direct and diffracted beams in a sufficiently perfect crystal permit the location of foreign atoms to be determined in the direction of the reciprocal-lattice vector, by monitoring secondary emissions in the form of x-ray fluorescence or other radiations. Three-dimensional locations can be determined for atoms below and above the surface, via triangulation of separate XSW measurements performed with nonparallel reciprocal-lattice vectors.[3] Quite high positional accuracy can be achieved— of the order of a few percent of the lattice spacing in favorable cases. The method has been applied to various surfaces and overlayer systems. In most applications substrate crystals were in the Bragg geometry with out-of-surface reciprocal-lattice vectors, where the incident and/or diffracted beams made large angles to the surface.

A geometry proposed by Cowan uses the grazing-incidence condition with reciprocal-lattice vectors nearly parallel to the surface[4] (Fig. 1). X rays at a small glancing angle ϕ_0 are diffracted by the bulk crystal during total external reflection, to produce a specular beam and a diffracted beam exiting into the incidence medium with small take-off angles. The x-ray field is more complicated here than in the Bragg geometry, involving incident, specular reflected, and Bragg diffracted beams outside the surface. The internal field is a coherent superposition of two Bloch waves. One Bloch wave (β or $j=1$ wave) has antinodes on the Bragg planes, and the other one (α or $j=2$ wave) has nodes on the planes.[5] The Bragg planes are located at the same positions as the peaks in the Fourier component of the electron-density distribution, and are thus defined without ambiguity. In general, any continuous change in the excitation of the two Bloch waves would result in a shift of a standing-wave pattern parallel to the reciprocal-lattice vector. In the grazing-angle geometry this can be controlled by either ϕ_0 or θ (Fig. 1). Unlike the Laue geometry in the absence of a specular reflection, the two Bloch waves are not always simultaneously excited. For example, when ϕ_0 is less than the critical angle for total external reflection, ϕ_c, only the $j=2$ wave can be excited.[4,6] This is because the incident wave vector has too large a component $K_{0\parallel}$ parallel to the surface to be continued by the $j=1$ wave. At $\phi_0 \ll \phi_c$, $K_{0\parallel}$ is even larger and the $j=2$ wave can no longer match it at θ less than the Bragg angle, θ_B. Consequently, no Bloch wave is produced for these incidence angles. The standing-wave behavior is thus complex with two, one, and zero Bloch waves produced depending on the incidence angles ϕ_0 and θ.[6,7] Discontinuous changes would occur at the limiting angles in a crystal without x-ray absorption. In real crystals the imaginary part of the dielectric susceptibility relaxes the situation and the transitions are not abrupt. Another feature of the grazing-angle x-ray-diffraction method is that the vacuum-diffracted wave, and hence the standing-wave field, become evanescent outside the surface for a certain domain of (ϕ_0,θ) with $\phi_0 > \phi_c$ and $\theta < \theta_B$.[4,6,7]

The grazing-angle XSW method allows the in-plane locations of surface atoms to be determined without a triangulation procedure. The x-ray fields only penetrate into shallow layers lying both just inside and outside the interface[4] making the geometry inherently sensitive to the in-plane surface structure. Standing-wave effects were first observed in the x-ray fluorescence[7-9] and electron emission[10] from lattice atoms of bulk crystals. The technique was then used to determine the registration of iodine adatoms with respect to Ge(111) surface atoms in the open-air environment.[11]

In this paper we present a grazing-angle XSW study of the Si(111):As-1×1 surface under ultrahigh vacuum (UHV) conditions. The arsenic-adsorbed Si(111) surface has been the subject of extensive structural and electronic studies in recent years and is of interest to surface scientists partly because arsenic deposition removes the 7×7 reconstruction of the clean Si(111) surface to yield a bulklike 1×1 surface, and partly because As passivates the silicon surface to produce a chemically stable surface. All experimental and theoretical data support the model with As atoms substituting for the silicon atoms at the

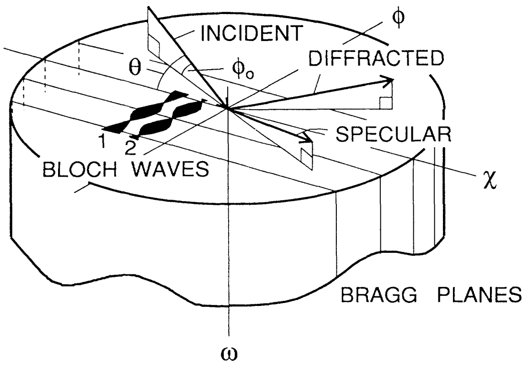

FIG. 1. Geometry for grazing-angle x-ray standing-wave measurements. An incident beam making a small angle ϕ_0 to the crystal surface and an angle θ to the Bragg planes which are nearly perpendicular to the surface creates two Bloch waves inside the crystal, and a specular reflected beam and a Bragg diffracted beam outside the surface.

topmost site of the Si(111) double plane.[12-15] An As atom is bonded to three second-layer silicon atoms, terminating the surface with a nonreactive lone-pair orbital.[12] The MEIS (medium-energy ion-scattering) studies indicate a highly ordered Si(111):As-1×1 surface, but there are indications of defect structures[14] and disorder[15] involved in the 1×1 surface. The stability of the As-terminated surface is limited. Prolonged exposure to hydrogen and ambient atmospheres disorders the surface, although it seems quite resistant to oxygen contamination.[12,13]

Our Si(111) substrates, $20\times17\times2.2$ mm^3, were prepared by polishing accurately oriented (111) crystals of silicon. The polished surface was chemically cleaned by the use of the Shiraki etch procedure.[16] After introduction into the UHV environment (2×10^{-8} Pa), the substrate was radiatively heated to 800 °C. Annealing for 3 h produced a sharp 7×7 RHEED (reflection high-energy electron-diffraction) pattern. The moderate annealing temperature was chosen to suppress the growth of silicon carbide, which was thought to affect the As ordering. The substrate while held at 800 °C was exposed to an arsenic beam from an outgassed effusion cell operated at 250–300 °C. The sample was then cooled to 400 °C in 30 min before the As shutter was closed. The pressure at the sample during this time was 6×10^{-5} Pa. This procedure is essentially the same as that employed by other authors to obtain a near-monolayer coverage of Si(111) by As.[13,14] Sharp 1×1 RHEED spots were observed from the sample at room temperature.

The arrangement for x-ray experiments was similar to previous grazing-angle diffraction experiments,[9,17] but with an important modification. The samples were prepared in a molecular-beam-epitaxy facility at the authors' institute, and transported to the Photon Factory in a pumped vessel, where they were transferred into an UHV x-ray-scattering chamber (4×10^{-7} Pa) via loadlock system. The chamber was equipped with swivels in air to control the inclination of an in-vacuum sample around the horizontal ϕ and x axes (see Fig. 1). The whole assembly was mounted on the vertical ω axis of a high-precision rotary table, which brought the $(\bar{2}20)$ planes perpendicular to the surface to the Bragg position. The chamber had beryllium windows to allow the specular reflected beam and the Bragg diffracted beam to reach separate x-ray detectors, and the fluorescent x rays to enter an energy-sensitive high-purity germanium detector.

X-ray data were collected on beam line 14B of the Photon Factory in Tsukuba. A beam of 16.84-keV energy was extracted from the superconducting vertical-wiggler source of synchrotron radiation by a slightly detuned double silicon monochromator. The harmonics-free beam was horizontally diffracted by a symmetric (220) silicon crystal, set in a nondispersive position for the sample $(\bar{2}20)$ planes. The output beam, limited by a 1 mm $(H)\times0.13$ mm (V) slit, was incident on the sample in the UHV chamber at a grazing angle such as to be diffracted by the $(\bar{2}20)$ planes with $\theta_B=11.05°$. Height adjustment allowed a part of the collimated direct beam to pass over the sample surface to reach a down-stream x-ray image detector. The linearly polarized synchrotron x rays with a vertical E vector greatly simplified the experiment: the sample could be placed in a horizontal position with the As-deposited (111) surface upward, and the optics involved only the σ waves. The photon flux of the specular beam was 10^6/s. The net x-ray fluorescence integrated over an energy range of the As $K\alpha$ line was of the order of 10 photons/s.

Figure 2 shows typical specular reflected (S), Bragg diffracted, and As fluorescence (F) intensities measured simultaneously as a function of deviation from the Bragg angle, $\Delta\theta=\theta-\theta_B$, for three values of ϕ_0 near the critical angle for total external reflection, $\phi_c=1.85$ mrad. We determined the ϕ_0 angles for these data at 1.1, 1.9, and 2.6 mrad from the separations of the direct and specular beams on the image detector. The specular and fluorescence data were normalized with the use of the intensities observed at θ far from θ_B at the same ϕ_0 angles. The observed $S(\Delta\theta)$ and $F(\Delta\theta)$ show similar profiles. The broken curves in Fig. 2 show the calculated $S(\Delta\theta)$ for a semi-infinite Si(111) crystal, while the solid curves show the calculated $F(\Delta\theta)$ for As atoms on the $(\bar{2}20)$ planes. These curves take into account the horizontal beam divergence $\delta\theta=10.1$ μrad due to the monochromator, as well as the vertical divergence $\delta\phi_0=0.20$ mrad corresponding to the 4σ source size of the synchrotron beam and the limited flatness of the sample crystal. The As atoms were assumed to lie 0.96 Å above the topmost bulklike silicon (111) layer,[13] although a 100% variation of the vertical height produced no appreciable effect on the emission profiles even at incidence angles where the diffracted beam was evanescent. The field intensities depended so weakly on the vertical position that visible changes occurred only after a displacement of 5–10 Å. This is consistent with the field extension of ~50 Å above the surface for such angles.[4,6,7] An error in ϕ_0 would explain the deviations of the calculated $S(\Delta\theta)$ and $F(\Delta\theta)$ in Fig. 2(b) for $\phi_0\sim\phi_c$, where the profiles depend more strongly on ϕ_0 than in other regions. The slightly broader experimental diffraction profiles than the calculations in Fig. 2 would indicate distorted near-surface layers in substrate silicon crystal. The previously reported abrupt drop of diffraction intensity to zero at negative $\Delta\theta$ (Refs. 8, 9, 11, and 17) was not observed at all ϕ_0's examined. This is accounted for by convolution effects.

Fluorescence yields from atoms at interplanar position x $(0 \leq x < 1.0)$ can be represented by $A + fB(x)$. Here A and $B(x)$ are proportional to the position-independent and -dependent terms of the standing-wave field, respectively, and f is the fraction of fluorescing atoms at x. It can be shown that A and $B(x)$ have similar amplitudes at $\theta \sim \theta_B$ and $\phi \sim \phi_c$. Figure 3 shows emission yields calculated for the As structures with f atoms on the $(\bar{2}20)$ planes and $(1-f)$ atoms at random positions. The calculations are made for $\phi_0 = 1.1$ mrad $(<\phi_c)$. An ordered structure $(f=1)$ with all As atoms on the $(\bar{2}20)$ Bragg planes $(x=0)$ shows a deep dip at $\Delta\theta \sim 0$, arising from the coincident nodal planes of the $j=2$ Bloch wave, which is the only Bloch wave contributing to the standing wave and has a minimum nodal electric-field strength at $\Delta\theta = 0$. A disordered structure $(f=0)$ with As atoms randomly occupying all x shows a distinct emission profile with a peak and a valley, representing the position-independent term A of the field intensity. Clearly, the yields observed from the sample in UHV are consistent with highly ordered As atoms with a coherent fraction f not less than 0.8. These are quite different from the As K yields observed from a less-ordered sample, shown by open circles in Fig. 3. The latter sample was prepared by a similar procedure, but exposed to air for a few days before the x-ray experiment. Combined with the previous Bragg XSW measurement in UHV,[13] the present grazing-angle result provides evidence for the high degree of positional coherence intrinsic to the As atoms chemisorbed on a clean Si(111) surface.

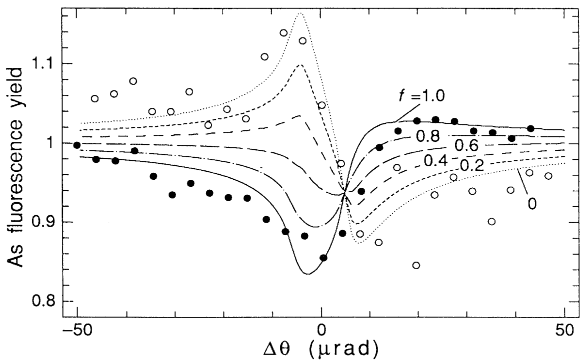

FIG. 3. Measured (circles) and calculated (lines) fluorescence yields at $\phi_0 = 1.1$ mrad. f represents the coherent fraction of the fluorescent As atoms on the Si $(\bar{2}20)$ planes. Closed circles denote data from a sample in UHV and open circles denote data from a disordered sample in open air.

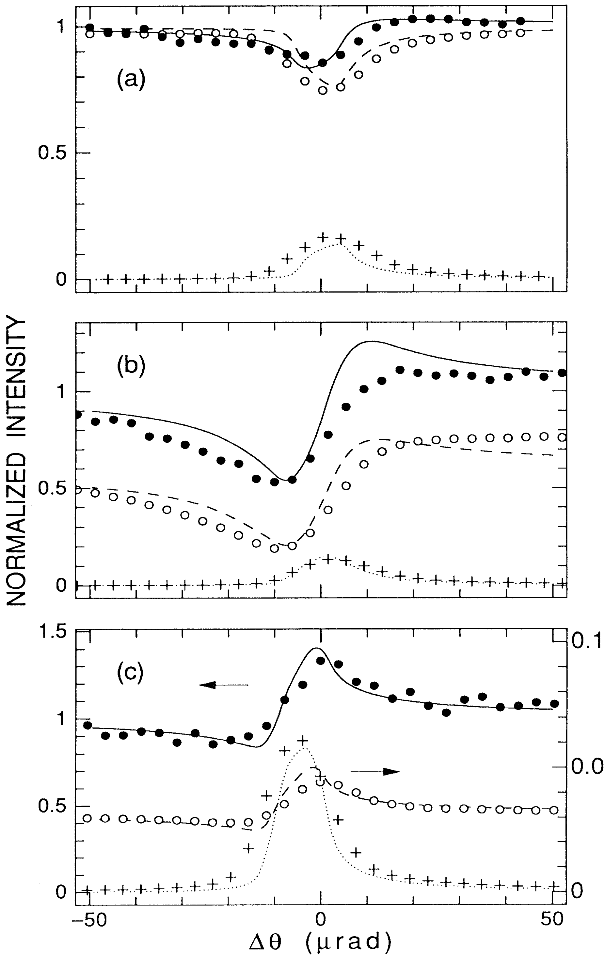

FIG. 2. Measured (symbols) and calculated (lines) reflectivities and As K fluorescence yields for the Si(111):As-1×1 surface in UHV at $\phi_0 = 1.1$ (a), 1.9 (b), and 2.6 mrad (c). Closed circles denote As K yields (F), open circles denote specular reflectivities (S), and crosses denote Bragg-diffraction reflectivities.

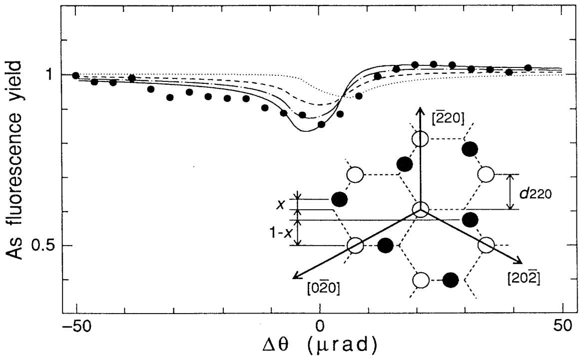

FIG. 4. Fluorescence yields observed from a sample in UHV (circles) and calculated for the 1:1:1 mixtures of the 0, x, and $1-x$ sites for As atoms with $x=0$ (solid curve), 0.1 (dash-dot curve), 0.15 (broken curve), and 0.2 (dotted curve). $\phi_0 = 1.1$ mrad. The inset shows the top view of the Si(111):As-1×1 surface with first-layer As atoms (closed circles) displaced off the $(\bar{2}20)$ planes by x. Open circles indicate second-layer Si atoms.

Fluorescence profiles from surface adsorbed atoms at $x=0$ show a marked change with f varying at a constant $\phi_0<\phi_c$. This is because the functional form of $B(0,\Delta\theta)$ is very dissimilar to that of $A(\Delta\theta)$ in this range of ϕ_0. The case is different with atoms at $x=0.5$. $B(0.5,\Delta\theta)$ has similar profiles to $A(\Delta\theta)$ for $\phi_0<\phi_c$, and hence the emission profile features remain essentially unchanged when f varies from 1 to 0. Decreasing f simply reduces the peak-to-valley ratio towards that of $A(\Delta\theta)$. At $\phi_0>\phi_c$, however, $B(0.5,\Delta\theta)$ shows a peak at $\Delta\theta\sim 0$ and a dip at $\Delta\theta\sim 0$, which make the $A+fB(0.5)$ profiles strongly f dependent. One can exploit this range of ϕ_0 to study the position and ordering of foreign atoms lying halfway between the Bragg planes.

The existence of a single site for the As atoms at the Si(111):As-1×1 surface was indicated by the simple As $3d$ spectra observed in core-level spectroscopy measurements.[12] The threefold symmetry of the Si(111) surface shows that if the As atom position is off the $(\bar{2}20)$ planes by x, positions 0 and $(1-x)$ are also occupied by As atoms (see inset in Fig. 4). Our grazing-angle XSW data indicate that multisite As adsorptions are unlikely. Figure 4 shows As fluorescence profiles for the mixed $0,x$, and $(1-x)$ sites calculated for $\phi_0=1.1$ mrad ($<\phi_c$) with $x=0.1$, 0.15, and 0.2. Equal As occupancies were assumed for the three positions to meet the symmetry requirement. Any departure of As atom location from the $(\bar{2}20)$ planes has effects on the profiles similar to that of disorder. Clearly, As position displacements greater than 0.1 in x are inconsistent with our XSW data. The conclusion is an acceptable one since a displaced As atom would break the equivalence of the three As-Si bonds at the Si(111):As-1×1 surface and produce strained bonds, which would be energetically unstable.

In summary, we have shown that grazing-angle x-ray standing waves can determine the in-plane location and ordering of surface adsorbed atoms in UHV. The high collimation and brilliance of synchrotron x rays obtained from an insertion-device source permitted monitoring the fluorescence from As atoms present in a monolayer coverage on the Si(111) surface. The characteristic dependence of the calculated emission profiles on the displacement and order parameters for x-ray glancing incidence angles smaller than ϕ_c allowed us to conclude, without sophisticated profile fitting, that the As atoms are located on the $(\bar{2}20)$ planes with little disorder. The observation is consistent with a bulklike surface with threefold-coordinated As atoms in the first layer.

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