X-ray standing-wave and tunneling-microscope location of gallium atoms on a silicon surface

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The position of gallium atoms on a silicon (111) surface has been completely determined using the tunneling microscope and x-ray standing-wave methods. The $(\sqrt{3}\times\sqrt{3})R30°$ electron diffraction pattern observed with $\frac{1}{3}$-monolayer coverages is shown to result from a simple adatom gallium lattice with the adatoms at a distance 1.49 Å above the bulk extrapolated surface (111) plane above the filled threefold silicon surface sites. Total-energy calculations correctly predict the binding site with the Ga 1.33 Å above the bulk (111) plane.

A knowledge of surface crystal structure is central to any attempt at a fundamental understanding of electrical, chemical, or mechanical properties associated with crystal surfaces. Progress in this area has been steady and impressive over the past several years with a number of new techniques becoming available to augment the classic role low-energy electron diffraction (LEED) has played in calling attention to a host of unanticipated structural effects on surfaces.

Increased interest has and will most certainly continue to shift from the study of clean self-terminated bulk crystals towards impurity terminated surfaces. In the following we present results of the first complete and conclusive study of such a case, gallium on silicon (111)-$(\sqrt{3}\times\sqrt{3})$. The complete solution to this problem is obtained by using two powerful methods, tunneling microscopy and x-ray standing-wave interferometry, to pinpoint atom location on the surface. The theoretical status of the field is then evaluated by comparison with local density approximation of density-functional theory.

Lander and Morrison[1] observed the classic adsorbed impurity-induced $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern induced on a silicon (111) surface more than 20 years ago. An explanation for this result in line with intuitive expectations, based on gallium's trivalency, would place the gallium atoms above three silicon atoms, themselves the last plane of a (111) silicon double layer. Such an arrangement of gallium atoms completely terminates all silicon surface dangling bonds with a coverage of $\frac{1}{3}$ monolayer (ML) (1 ML$=7.83\times10^{14}$ atoms/cm^2). While alternative structures may be envisioned, even this simple adatom model has nontrivial alternatives for the gallium atom positions because there are two types of threefold triangular sites above the surface. The first, the so-called hollow of H_3 (Ref. 1), has no atom directly below in the lower part of the (111) silicon surface double layer. The other site, the T_4, is also triangular but contains a silicon atom directly in the bottom of the double layer.

The T_4 model is very nonintuitive. If lattice relaxations are not allowed then an adatom in a T_4 site is prevented, by the presence of the second layer atom, from being close enough to the first layer atoms to form strong bonds. However, for the Si(111)-$(\sqrt{3}\times\sqrt{3})$:Al surface first-principles total energy calculations[2] predicted that, in fact, the T_4 site was lower in energy than the H_3 site by 0.3 eV per adatom. Although there is now strong evidence, based on transmission electron diffraction[3] and tunneling microscopy,[4,5] that Si adatoms on the Si(111)-(7×7) surface occupy the T_4 sites, no such conclusive experimental determination of the bonding site has been made for the group-III adatoms on Si(111). Thus the generality of the T_4 site for adatom bonding on Si(111) is an open question.

Our study was designed to directly answer that question for the case of gallium. In Fig. 1 we present tunneling images for Ga on Si(111). The sample from which this image was obtained was prepared by evaporating gallium atoms from an oven in the UHV chamber in a manner that yielded regions of both (7×7) and $(\sqrt{3}\times\sqrt{3})$ reconstruction when viewed with LEED. After much searching over regions that were either (7×7) or $(\sqrt{3}\times\sqrt{3})$ the region shown in Fig. 1(a) was discovered. The bottom of the figure and middle–left-hand side show the simple $(\sqrt{3}\times\sqrt{3})$ reconstruction characteristic of local $\frac{1}{3}$ ML gallium coverage, while the remainder of the adatom structure is characteristic of the (7×7) clean silicon surface. As pointed out by one of us previously,[6] such a picture allows the lateral registration of an unknown surface lattice, the gallium $(\sqrt{3}\times\sqrt{3})$ in this case, to be determined by comparison with the known adatom site on the Si (7×7) surface. A similar procedure was used by Wilson and Chiang[7] to assign the lateral position of Ag on Si(111) apparently H_3, without a determination of surface normal coordinates or indepen-

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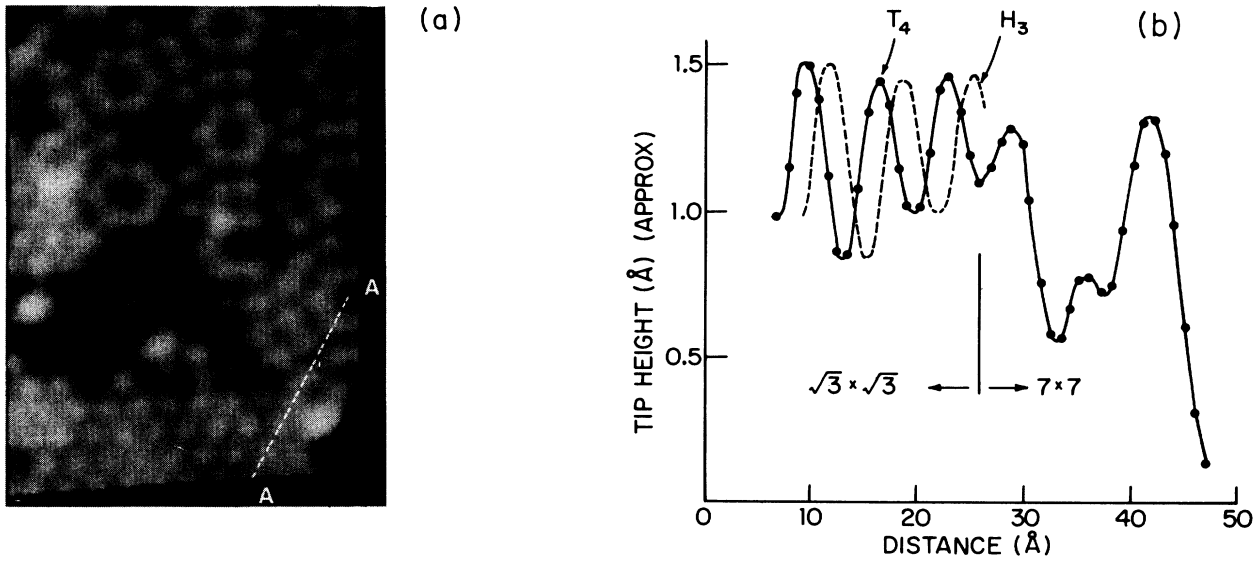

FIG. 1. (a) Tunneling imaging showing (7×7) and $(\sqrt{3}\times\sqrt{3})R30°$ reconstructions on a partially gallium covered silicon (111) surface for tip bias of −1.1 V and tunnel current of 1 nA. (b) Line scan of top height along the A-A section shown in Fig. 1. The dotted line shows how scan would look for H_3-type reconstruction. Heights of atoms in $(\sqrt{3}\times\sqrt{3})$ are similar to (7×7), confirming the adatom model.

dent confirmation of the chemical species actually imaged. Lateral distance measurements in Fig. 1(b) show unambiguously that (i) the adatom structure for the gallium is correct (the fact that we are imaging Ga atoms on the top layer is established by the standing wave results) and (ii) the T_4 site is populated by gallium atoms. The adatom structure is similar to the $(\sqrt{3}\times\sqrt{3})$ lattice observed by Nogami *et al.*[8] for indium on silicon. The assignment of the *lateral site* is the new result for these structures.

The goal of quantitatively locating the gallium atoms perpendicular to the silicon surface was achieved by the powerful method of x-ray standing-wave interferometry.[9–11] Here an x-ray standing wave field at a crystal surface is excited through interference between an incident x-ray plane wave and the Bragg diffracted wave scattered from the crystal below the surface. The intensity of the standing wave field has the periodicity of the bulk diffracting planes; in our case the (111) planes parallel to the surface were chosen. In addition, and most importantly, as one scans the incident beam angle through the small range corresponding to total Bragg reflection, the phase of the diffracted beam shifts by π, making the phase of the standing wave field shift by π relative to the crystal lattice below. This ability to experimentally move the x-ray standing-wave field in space (in this case, perpendicular to the surface), in a known quantitative way, is the basis of our ability to locate atoms accurately. The x-ray fluorescence signal from gallium atoms monitored as a function of standing-wave phase allows a prediction of position relative to the lattice below with the use of a two-beam dynamical theory calculation that is simple and accurate.

For the x-ray measurements, $\sim\frac{1}{3}$ ML coverage was used and the surface was observed to completely transform by LEED from the (7×7) to $(\sqrt{3}\times\sqrt{3})$ reconstruction with deposition on the silicon surface at 550 °C. The coverage was determined by x-ray fluorescence scattering using an ion-implanted calibrated reference which was in turn calibrated using Rurtherford backscattering.

Figure 2 shows the results of the UHV x-ray standing-wave measurements. The data points show the angular dependence of gallium fluorescence yield and the Bragg reflectivity of the incident Mo $K\alpha$ radiation. The solid lines are theoretical fits to the dynamical theory. Excellent fit to the reflectivity is obtained with no adjustable parameters and is characteristic of the highly quantitative capability of the method. The fit to the fluorescence is obtained with two adjustable parameters. The first, called the position parameter $P=0.59$, gives the Ga posi-

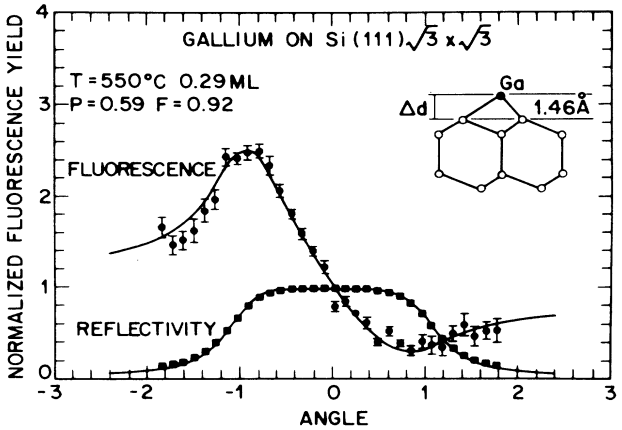

FIG. 2. Reflectivity and fluorescence yield for Ga on Si(111)-$(\sqrt{3}\times\sqrt{3})R30°$. Inset shows [110] projection of (111) planes with Ga in the T_4 geometry.

tion in dimensionless units relative to the bulk extrapolated surface plane. In terms of the Si d_{111} spacing (3.136 Å) this corresponds to a Ga atom height of 1.46±0.03 Å. The inset in Fig. 2 shows Ga in the T_4 site and its height above the upper half of the bulk extrapolated Si(111) plane. From several measurements under a variety of depositions we have established an average Ga position at 1.49±0.03 Å.

The second parameter F, called the coherent fraction, has a value 1 when all fluorescing atoms are on identical lattice plane positions relative to the (111) electron density distribution in the crystal. While the position parameter P is not sensitive to deposition conditions, the coherent fraction F depends on preparation details. The maximum experimental value $F=0.97$ indicates that only one vertical position uniquely explains the data.

In vivid contrast to the direct determination of the Ga position with standing waves, we point out the ambiguity that can arise with conventional diffraction methods. In two successive papers Kawazu *et al.*[12] using the same LEED data for $(\sqrt{3}\times\sqrt{3})$ Ga on Si, have arrived at two entirely different structures for Ga on Si, the first with Ga on substitutional sites and the second in the T_4 configuration.

Anticipating the theoretical calculations below we note that the difference between vertical positions of adatoms in H_3 versus T_4 sites is expected to be of order 0.2–0.3 Å (see below). The x-ray results we present are more than adequate to establish the height to such accuracies and together with calculations could in principle establish which site is occupied. Using the tunneling data the atom location becomes a totally experimental process so that a comparison with theory is a test of the latter.

The measured Ga position in the $\sqrt{3}$ structure will now be compared with positions calculated for the T_4 and H_3 geometries which are indicated in Table I. Total energy calculations have been carried out as in Ref. 2 using the local-density-functional approach and employing the momentum space pseudopotential formalism. Centrosymmetric supercells containing eight layers of Si and two layers of Ga were employed. The equilibrium geometries for the two surface structures were obtained using the Hellmann-Feynman theorem to find the minimum energy configuration for both. The T_4 geometry was found lower in energy than the H_3 by 0.38 eV per adatom.

Substantial subsurface relaxations are predicted for both models. The calculated displacements of the Si substrate atoms are quite significant and play a major role especially in the T_4 site having the lower energy. These relaxations are indicated in angstroms from the bulk silicon positions, in Table I for both models. In the T_4 geometry the Ga position is predicted to be 5.25 Å above the fifth layer atoms which were kept fixed in the calculation. Measured relative to the bulk extrapolated surface plane the T_4 corresponds to a height of 1.34 or 0.16 Å smaller than the x-ray determination. The position for the H_3 configuration is lower and corresponds to a height of 1.17 or 0.34 Å below our measured value.

Considering the large subsurface relaxations involved, the position calculated for the Ga atom in the T_4 model is in fairly good agreement with experiment. In assessing the accuracy of the calculation, one must keep in mind that to obtain the correct Ga position [relative to the bulk (111) planes], the calculation must give the displacements of all the underlying Si layers correctly. For Si(111)-$(\sqrt{3}\times\sqrt{3})$:Ga there are four layers involved in the reconstruction. Thus it is understandable that the accuracy obtained here is not quite as good as for Si(111)-(1×1):As,[11] where only 1 layer is involved.

In summary this work provides the first direct and quantitative determination of the gallium adatom position on Si(111)-$(\sqrt{3}\times\sqrt{3})$. The method used should prove of general applicability in solving surface impurity problems. Considering the complexity of the substrate relaxation for the case studied here the agreement between calculated and measured gallium vertical position is encouraging.

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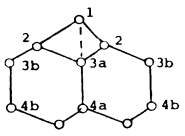
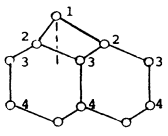
TABLE I. Substrate relaxations for the T_4 and H_3 sites. δr positions are with respect to axis through the T_4 and H_3 sites. δz refers to the unrelaxed position. δr and δz are in angstroms.

	T_4		H_3	
Ga atom position	δz	δr	δz	δr
2	−0.04	−0.15	−0.16	−0.07
3*a*	−0.35	0	−0.12	−0.03
3*b*	0.12	0		
4*a*	−0.23	0	−0.08	−0.03
4*b*	0.08	0		
[1$\bar{1}$0] projections of (111) planes for T_4 and H_3 sites				

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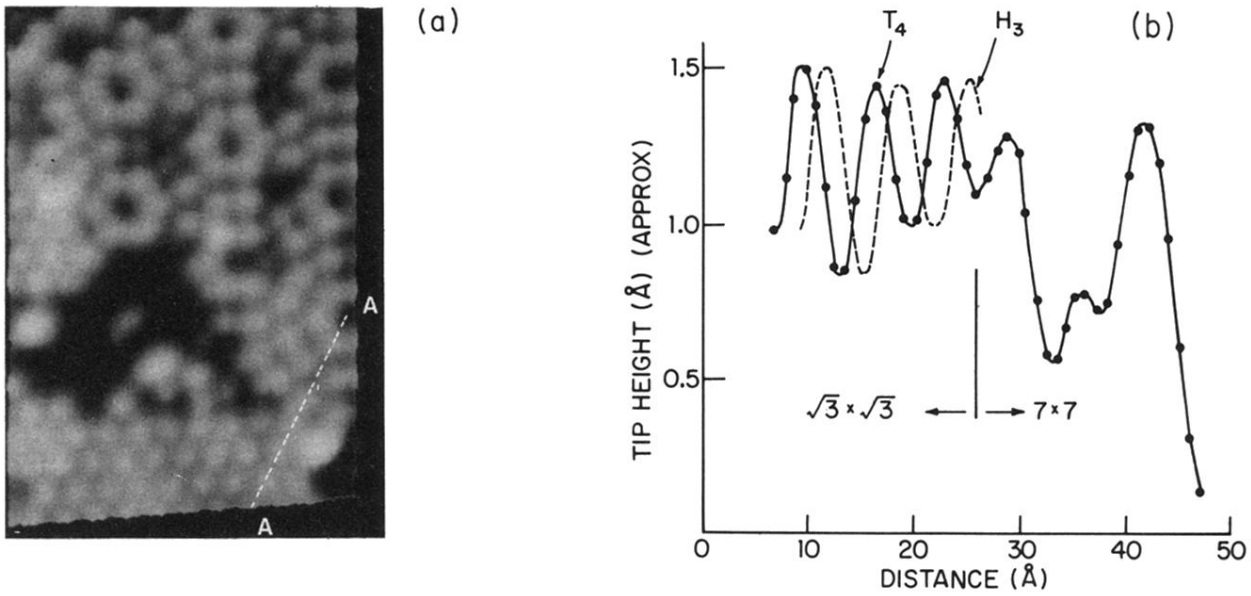

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