# Geometric structure of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface

Akira Kawazu and Hiroshi Sakama

*Department of Applied Physics, The University of Tokyo, 7-3-1, Hongo, Tokyo, 113 Japan*
(Received 14 August 1987)

The structure of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface has been studied by dynamic analysis of low-energy electron-diffraction curves of intensity versus energy ($I$-$V$). It has been found that a structure in which Ga atoms are located on the second layer of Si atoms well explains the experimentally obtained $I$-$V$ curves. In this geometry, a large deformation of the surface layer results from the stable adsorption of Ga atoms. The optimum configuration is close to that proposed by Northrup in his study of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface.

Among the reconstructed surface structures which are formed on the (111) surface of crystals with fcc or diamond structures, the $\sqrt{3}\times\sqrt{3}$ structure is the most frequently observed, and many experimental and theoretical studies related to it have already been published.[1] However, in only a few cases has the geometry of the surface been successfully determined. In most cases, this is mainly due to inadequate use of the methods of measurement. In the case of low-energy electron-diffraction (LEED) studies, sufficient data to determine the surface geometry can be obtained by measuring the intensity-energy ($I$-$V$) curves of diffracted beams.[2] Shortcomings of LEED analyses include the necessity of complicated calculations and the considerable computing time required to perform this kind of calculation.[3,4] However, recent advances in computer technology enable us to study reconstructed surface structures whose surface unit cells contain fairly large numbers of atoms.

In this study we report the results of dynamic analysis of the $I$-$V$ curves of LEED from the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface.

We used $n$-type silicon wafers of high resistivity ( > 10 kΩ cm), cut to within 1' parallel to the (111) plane, as substrates. A molecular beam of Ga from a Knudsen cell was impinged on the silicon surface. The saturation coverage of Ga atoms for the $\sqrt{3}\times\sqrt{3}$ structure has been determined as $\frac{1}{3}$ of a monolayer by quadrupole mass spectroscope observation of the increase in intensity of the desorption flux of Ga atoms from the Si surface after the completion of the $\sqrt{3}\times\sqrt{3}$ phase at high substrate temperatures, and by observing the break points in curves of Auger-electron-spectroscopy signal versus deposition time.[5,6] When $\frac{1}{3}$ of a monolayer of Ga atoms was deposited at 740 K, an unambiguous Si(111)$\sqrt{3}$ $\times\sqrt{3}$ structure was observed. $I$-$V$ curves from the Si(111)$\sqrt{3}\times\sqrt{3}$ surface have been obtained by measuring the brightness of the bright spots on the fluorescent screen by means of a spot photometer. The calculations of $I$-$V$ curves were performed using a renormalized forward-scattering algorithm.[4] The scattering matrices for nonequivalent composite layers were calculated by a matrix inversion formalism, and the intensity of the beams reflected from a stack of these composite layers

was obtained by the renormalized forward scattering perturbation method. The computer programs developed by Pendry[3] and by Tong and van Hove[4] were modified to apply to cases in which the substrate layers consisted of composite layers.[7] Further modifications were made when we used vector processors (Hitac S-810, Hitachi Ltd.).

We have measured $I$-$V$ curves for nine beams, the (1 0), (0 1), (2 0), (1 1), (2 −1), $(\frac{1}{3} \ \frac{1}{3})$, $(\frac{2}{3} \ -\frac{1}{3})$, $(\frac{2}{3} \ \frac{2}{3})$, and $(\frac{4}{3} \ -\frac{2}{3})$ beams. Among these observed $I$-$V$ curves, those of the $(n/3 \ n/3)$ and $(2n/3 \ -n/3)$ beams coincide to within experimental error. The crystal structure of bulk Si shows threefold symmetry about the [111] axis. Hence the diffraction beams from the surface should also show threefold symmetry when the electron beam is incident normal to the surface. The observed sixfold symmetry of the above series of diffraction beams implies
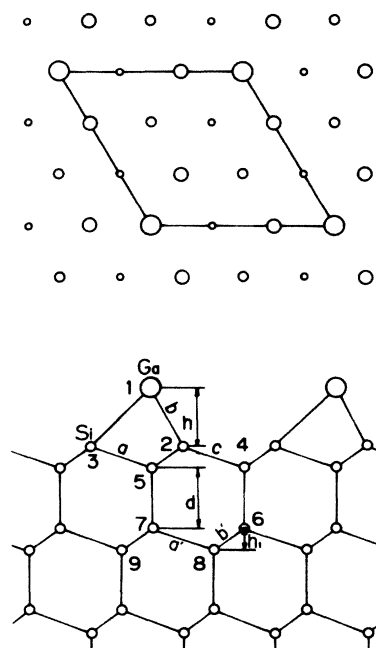


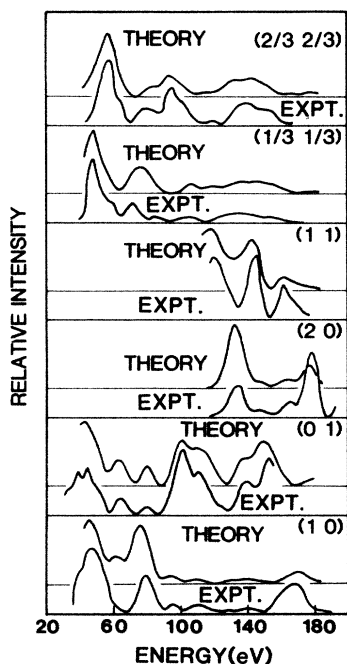FIG. 1. Top and side views of the surface structural model.

    

FIG. 2. Comparison of calculated and experimental LEED
I-V spectra for the optimized configuration.

that Ga atoms are located at special adsorption sites on
the Si substrate; this must be taken into consideration
when we choose a structural model for the surface. The
structural model proposed here satisfies this condition.

The agreement between calculated and experimentally
obtained I-V curves was judged both by visual inspection
and using the reliability factor (R factor) proposed by
Zannazi and Jona.[8]

Figure 1 shows the structural model for which calcu-
lations were performed. In this model, $\frac{1}{3}$ of a monolayer
of Ga atoms is located on the hollow site above the
second-layer Si atoms (we shall call this the HL2 site).
We varied the eight structural parameters shown in Fig.
1 which are related to the first and the second composite
layers. These are (1) the Ga—Si bond length b, (2) the
bond length a between atoms 3 and 5, (3) the bond
length c between atoms 2 and 4, (4) the distance h be-
tween Ga and the first Si layer, (5) the distance d be-
tween the first and the second composite Si layers, (6)
the bond length a' between atoms 7 and 8, (7) the bond
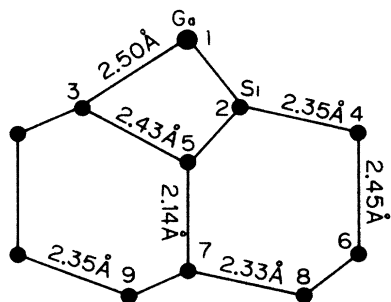length b' between atoms 6 and 8 in the second composite

FIG. 3. Side view of the optimized surface geometry.

TABLE I. The atomic coordinates for the optimum
configuration shown in Fig. 3. The x, y, and z axes are parallel
to the [$\bar{1}\bar{1}1$], [$\bar{1}2\bar{1}$] and [$\bar{1}01$] directions, respectively.

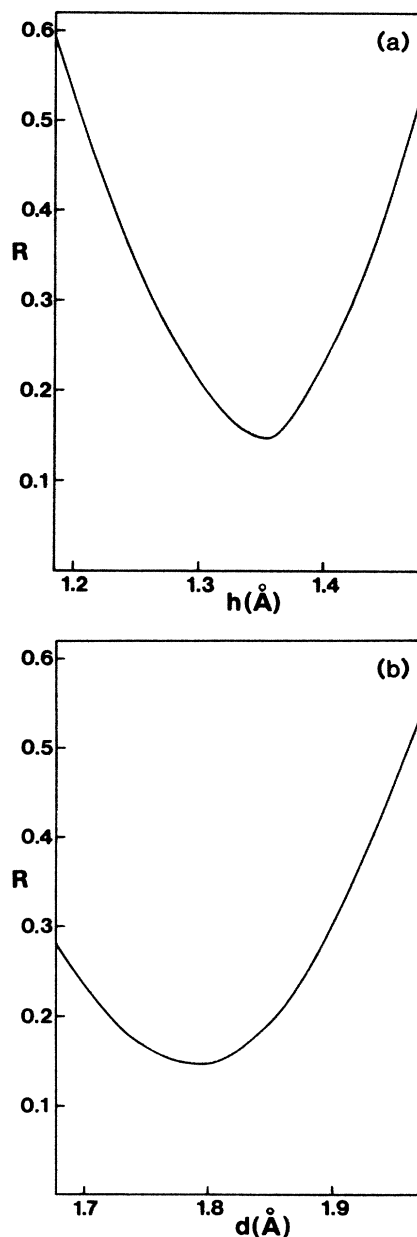| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| 1 | 0.00 | 0.00 | 0.00 |
| 2 | 1.35 | 1.05 | 1.83 |
| 3 | 1.35 | −2.10 | 0.00 |
| 4 | 1.93 | 3.33 | 1.92 |
| 5 | 2.57 | 0.00 | 0.00 |
| 6 | 4.37 | 3.33 | 1.92 |
| 7 | 4.71 | 0.00 | 0.00 |
| 8 | 5.22 | 2.27 | 0.00 |
| 9 | 5.22 | −1.13 | 1.97 |

FIG. 4. Variation of the R factor as a function of the dis-
tance (a) between the Ga atoms and the first Si layer, and (b)
between the first and the second composite layer.

layer, and (8) the distance $h_1$ between atom 6 and the fourth Si layer.

The procedure used to adjust the structural parameters was as follows. First the five parameters related mainly to the first composite layer were changed; that is, $a$, $c$, and $d$ were varied around the value for the bulk material, 2.35 Å, and $b$ and $h$ were varied around the sum of the atomic radii of Ga and Si, 2.40 Å. After we obtained fairly good agreement between experimental and theoretical $I$-$V$ spectra, we then added the three other structural parameters to be adjusted, $a'$, $b'$, and $h_1$, which are related to the second composite layer. We have calculated the $I$-$V$ curves for about 5500 different parameter combinations. The experimental and theoretical $I$-$V$ curves for the optimum atomic configuration are compared in Fig. 2. The agreement for this set of parameters is good for all observed $I$-$V$ curves, and a sufficiently low $R$ factor of 0.15 was obtained. The side views of this configuration are shown in Fig. 3, and atomic coordinates are listed in Table I.

Figure 4 shows changes in the Zannazi-Jona $R$ factor as the structural parameters are varied. In all cases, the other parameters were kept fixed at the optimum values shown in Table I. The $R$ factor is sensitive to the values of $h$ and $d$, and this implies that the values of these parameters can be determined precisely by LEED studies.

When Ga atoms are stably adsorbed onto the HL2 site above the second-layer Si atoms, keeping the distance between atom 1 (Ga) and atom 2 nearly equal to the sum of the atomic radii of Ga and Si, a large deformation must be introduced into the surface layer of the silicon, because without such a deformation the distance between atoms 1 and 5 would become too short. It is easily seen from Figs. 1 and 3 that in the deformed surface layer, atoms 2 and 3 should move toward the normal axis which passes through the center of the Ga atom, atoms 4 and 6 toward the topmost surface, and atoms 5 and 7 away from the surface. As a result, the bond length between atoms 4 and 6 is elongated, and that between atoms 5 and 7 is shortened, relative to the bulk value. The optimum geometry for adsorption onto the HL2 site obtained in the present LEED study meets all these conditions, and the values of the structural parameters are reasonable ones judging from Fig. 3 and Table I.

We can thus conclude that the actual surface geometry of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface is that shown in Fig. 3 in which $\frac{1}{3}$ of a monolayer of Ga atoms is adsorbed onto HL2 sites, on the basis of the sufficiently low $R$ factor and the above surface deformation. This surface structure is also proposed as capable of explaining the surface properties of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface reported by Northrup.[9]

We have performed the calculations for four other structural models,[10] changing their structural parameters; i.e., models in which (1) Ga atoms are located in the hollow sites above the fourth-layer Si atoms, (2) Ga atoms are sitting on clusters composed of three Si atoms, the center of which are located above second-layer Si atoms, (3) clusters are located above fourth-layer Si atoms, and (4) Ga atoms are substituted for $\frac{1}{3}$ of the Si atoms in the topmost Si layer. The minimum $R$ factors for these models are 0.34, 0.45, 0.45, and 0.25, respectively. Even for the substitutional model in which the lowest $R$ factor has been obtained, fairly good agreement between experimental and theoretical curves has been obtained only for (1 0) and (0 1) beams.

In summary, we have compared experimental and theoretical LEED $I$-$V$ spectra for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface. We have shown that on the Si(111) surface, Ga atoms are located at hollow sites above the second-layer Si atoms. The optimum surface configuration obtained agrees with the large deformation of the substrate surface expected to occur when adsorbed Ga atoms combine with the topmost Si atoms, assuming reasonable values for bond lengths. This study shows that LEED analysis is very efficacious for determining the atomic configuration of a reconstructed surface. This is especially true when this method is applied together with scanning tunneling microscopy,[11] because the latter method gives us the surface morphology.

[1]For example, see R. J. Wilson and S. Chiang, Phys. Rev. Lett. **58**, 369 (1987); E. J. van Loenen, J. Demuth, R. M. Tromp, and R. J. Hamers, *ibid.* **58**, 373 (1987), and references therein.

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