PHYSICAL REVIEW B VOLUME 42, NUMBER 12 15 OCTOBER 1990-II

Atomic structure of Si(111)-($\sqrt{3}\times\sqrt{3}$)R 30°-Al studied by dynamical low-energy electron diffraction

H. Huang and S. Y. Tong
Department of Physics and Laboratory for Surface Studies, University of Wisconsin–Milwaukee,
P.O. Box 413, Milwaukee, Wisconsin 53201

W. S. Yang,* H. D. Shih,† and F. Jona
Department of Materials Science and Engineering, State University of New York, Stony Brook,
Stony Brook, New York 11794-2275

(Received 15 May 1990)

We have carried out a quantitative low-energy electron-diffraction intensity analysis of a Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Al structure. We found that Al atoms on a $\sqrt{3}\times\sqrt{3}$ array are absorbed on the threefold-symmetrical sites above the Si atoms in the second layer of the Si{111} surface. Atomic coordinates and bond lengths have been determined for the Al overlayer and all atoms in the first three layers of the substrate. With this model, some surface bonds are stretched by 3.4% (maximum), while others are compressed by 5.1% (maximum).

The atomic structure and bonding of metal overlayers on semiconductor surfaces are of great interest to both science and technology because of their importance in influencing properties of metal-semiconductor interfaces. The superstructure obtained by the reaction of Al with a Si{111} surface, the so-called Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Al phase, is a prototypical metal-semiconductor interface which has been studied with a variety of surface-sensitive techniques: low-energy electron diffraction (LEED),[1,2] angle-resolved photoemission spectroscopy,[3–6] inverse-photoemission spectroscopy,[7] electron-energy-loss spectroscopy,[2] scanning tunneling spectroscopy,[8,9] and band-structure–total-energy-minimization calculations.[10] However, the precise atomic structure of this phase is still unknown.

At an Al coverage of $\frac{1}{3}$ the most natural model for the $\sqrt{3}\times\sqrt{3}$ overlayer is one in which Al atoms adsorb on threefold-symmetrical sites over a bulklike Si{111} lattice.[1] In this model, each Al adatom, which has three valence electrons, saturates three Si dangling bonds. By arranging the Al adatoms in a $\sqrt{3}\times\sqrt{3}$ geometry, complete saturation of all silicon dangling bonds is achieved by $\frac{1}{3}$ of a layer of Al. There are, however, two different types of threefold-symmetrical sites on Si{111}, one above the Si atom in the fourth layer (H_3 sites) and one above the Si atom in the second layer (T_4 sites).

Originally, Lander and Morrison[1] proposed an adatom model in which the Al atoms occupy the H_3 sites. An alternative geometry was suggested by a theoretical study of Northrup[10] with the Al adatoms bonded to three first-layer Si atoms in the T_4 sites, as these sites were found to be more stable than the H_3 sites by 0.3 eV/adatom.

The tunneling-spectroscopy results[8,9] and the photoemission results[3–7] favor the T_4 site over the H_3 site. This preference is also based on Northrup's calculation,[10] which predict a band gap of 1.5 eV for the T_4 model, but only 0.8 eV for the H_3 model. The band gap of nearly 2 eV as observed by tunneling-spectroscopy and photoemission measurements is significantly larger than Northup's prediction for either model, but is closer to the predictions for the T_4 model. Additional support for the T_4 model is provided by experimental measurements of the band dispersions for both occupied and unoccupied states,[3–7] which show better agreement with the T_4 model than with the H_3 model. Thus, it appears likely that the T_4 site is the correct adsorption site for the Al adatoms.

We report here the results of a quantitative dynamical LEED intensity analysis of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Al structure which confirms T_4 as the correct adsorption site and also determines the positions of Al adatoms and all atoms in the first three layers of the substrate. The reliability of LEED for quantitative structure analysis of surface structures has been demonstrated repeatedly since the early 1970s,[11,12] and has recently been reconfirmed by the successful determination of structural reconstructions on a number of complex clean and metal-covered semiconductor surfaces.[13–17]

The experiment required first the preparation of a clean and well-crystallized Si{111} surface. For this purpose, a Si{111} wafer (n-type) was heated in vacuum (1×10^{-10} Torr) to about 1400 °C for 50 min. producing thereafter a sharp 7×7 LEED pattern. Al was then deposited on this surface from a source consisting of a bead of pure Al metal melted on a W spiral which was heated electrically. During deposition the clean Si{111} surface was heated to about 800 °C. Typically, Al amounts equivalent to three or four atomic layers were deposited (after deposition, the 7×7 LEED pattern was still visible, but with very high background), then the sample was heated to about 1000 °C for 30 min, producing a sharp $\sqrt{3}\times\sqrt{3}$ pattern with low background. LEED intensity data of eight beams were collected with a television-camera system described elsewhere.[18] The data were then normalized to constant incident electron current and corrected for the contact-potential difference between sample and electron gun cathode (3.6 eV), and the background was subtracted.

The dynamical LEED calculations were performed using the real- and reciprocal-space symmetrized LEED code described elsewhere.[13,14,19] The positions of the atoms in five surface planes [the adatom plane, and two (1×1)-like double layers below] were varied, while deeper-lying Si atoms were held at bulk positions. The positions of the fourth-layer Si atoms were found to be very close to bulk sites, and these were set to bulk positions in the final result. With the C_{3v} point-group symmetry at normal incidence, the symmetrized LEED code selects one adatom and three substrate atoms (instead of six) per $\sqrt{3}\times\sqrt{3}$ cell in each of the two double layers in the surface region. The multiple-scattering calculations used six partial waves, a constant linear potential of 7 eV and an imaginary potential of 4.25 eV to simulate the effect of inelastic scattering.

Three structure models were tried: two overlayer models in which Al was placed as an adatom on H_3 and T_4 sites, respectively, and a substitutional model (no adatoms) in which every one out of three surface Si atoms was substituted by Al. To achieve best agreement between theoretical and experimental (I-V) spectra, the structural parameters for each model were varied so as to minimize the r factor.[20] The best fit to experiment was achieved with an optimized T_4 structure which produced an r factor of 0.177. The other two models had much higher reliability (r) factors and could be easily ruled out. Figures 1 and 2 show the comparison of theoretical and experimental (I-V) spectra for the optimal T_4 structure with the individual r factor for each beam indicated.

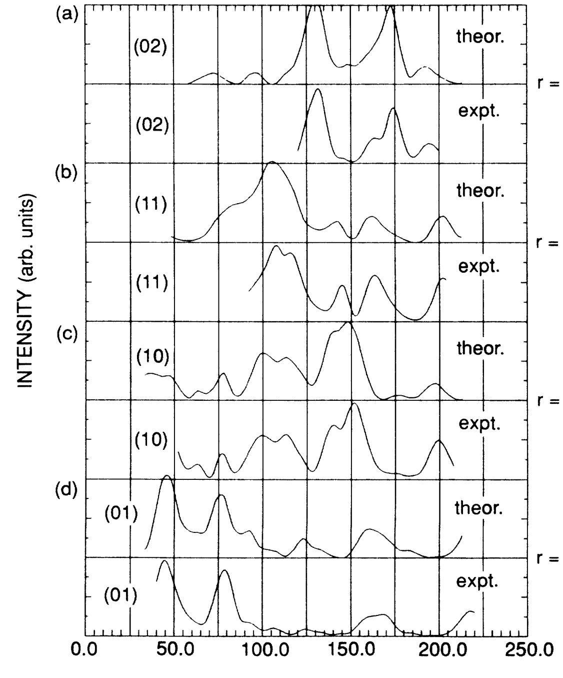

FIG. 1. Comparison between theory and experiment for the optimal T_4 model; the integral-order beams are shown.

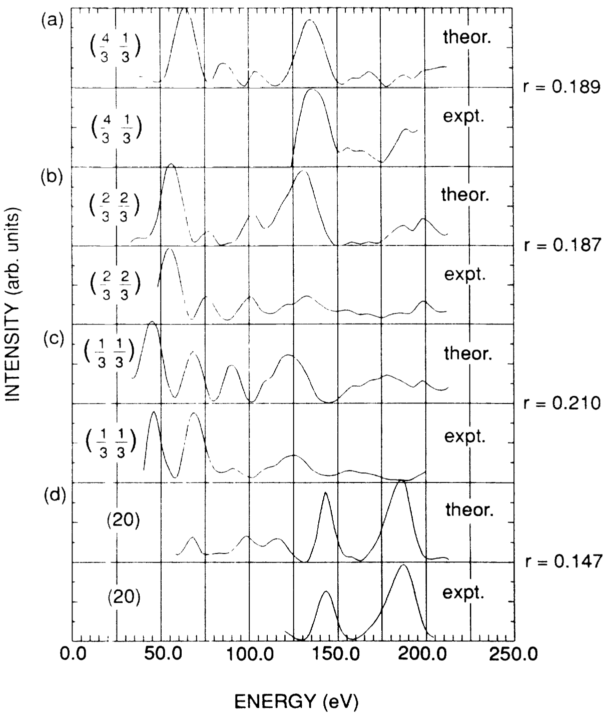

FIG. 2. Comparison between theory and experiment for the optimal T_4 model, showing one integral-order beam and three fractional-order beams.

The atomic displacements from the 1×1 bulk coordinates of the Si atoms in the optimal T_4 structure are indicated in Fig. 3. The major relaxations are the following: the three Si atoms in the first layer relax radially inwards by 0.15 Å and up by 0.02 Å, the Si atom in the second layer directly below the Al adatom relaxes by 0.44 Å downwards, and the Si atom further down in the third

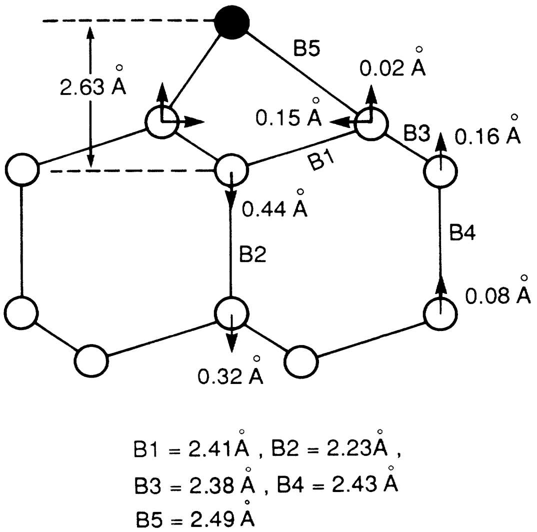

FIG. 3. The preferred Si(111)-$(\sqrt{3}\times\sqrt{3})R30°$-Al structure, with Al (solid circle) occupying the T_4 site. Arrows refer to atomic displacements from bulk sites.

TABLE I. Bond-length change for Al at T_4 adatom site.

Bond	Species	Length	Bulk value	Compression (−) or extension (+)
$B1$	Si—Si	2.41	2.35	+2.6%
$B2$	Si—Si	2.23	2.35	−5.1%
$B3$	Si—Si	2.38	2.35	+1.4%
$B4$	Si—Si	2.43	2.35	+3.4%
$B5$	Si—Al	2.49	2.60	−4.2%

TABLE II. Bond-length change for Al at B_5 substitutional site.

Bond	Species	Length	Bulk value	Compression (−) or extension (+)
$B1$	Si—Al	2.41	2.60	−7.3%
$B2$	Si—Al	2.23	2.60	−14.1%
$B3$	Si—Si	2.38	2.35	+1.4%
$B4$	Si—Si	2.43	2.35	+3.4%
$B5$	Si—Si	2.49	2.35	+5.9%

layer is pushed downwards by 0.32 Å. The other two Si atoms in the second layer move upwards by 0.16 Å, and the atoms bonded to them in the third layer are pulled upwards by 0.08 Å. The distance between the Al adatom to the Si atom directly below it is 2.63 Å—much larger than the bond length between Al and the three first-layer Si atoms, 2.49 Å (i.e., $B5$ in Fig. 3). This would indicate that the interaction between the Al adatom and the second-layer Si atom directly below in the T_4 adsorption topology is weaker than that between the Al adatom and the first-layer Si atoms. Of the four Si bonds ($B1$,$B2$,$B3$,$B4$), we found that $B2$ is compressed, while the other three are stretched. The bond-length changes are small, in the order of ±0.1 Å—several times smaller than the largest atomic displacement 0.44 Å. Thus, we see that atomic relaxation plays a very important role in surface reconstruction: the Si atoms in the first two bilayers move around to release the strain energy caused by the Al-adatom T_4 adsorption topology. Table I lists the percentage changes in the surface bond lengths for the Al-adatom geometry.

It is important to note that, while the atomic positions and interatomic distances in the surface region are determined with confidence, the LEED analysis could not rule out random substitution of the Si atoms by Al, *as long as the surface structure remains unchanged.* This is because substitution of Al at random Si sites does not affect the LEED (I-V) spectra; it would only increase the diffuse background. Indeed, even if we interchange Al and Si atoms in ordered arrays, the effect on the I-V curves will be small. This is because Al and Si are neighbors in the Periodic Table, and the scattering factors from their core regions (the part most important to LEED) are very similar. For example, we have interchanged the locations of Al and Si atoms, placing $\frac{1}{3}$ monolayer ML Si atoms at adatom positions and $\frac{1}{3}$ ML Al atoms in the second layer directly below (the so-called "B_5 position;" see, e.g., Ref. 17). We obtained essentially the same calculated I-V curves as depicted in Figs. 1 and 2, *as long as the structure is held unchanged.* However, since the covalent radius of Al (1.43 Å) is 22% larger than that of Si (1.17 Å), it is highly unlikely that a great deal of substitution (ordered or random) would take place without resulting in substantial structural relaxation. Also, substitution without structural relaxation would greatly increase the surface strain energy. For example, in Table II we list the bond-length change for Al in the B_5 site. In this configuration, the bonds $B1$, $B2$, and $B5$ are stretched or compressed substantially more than the case of Al adatoms. The largest change is in the $B2$ bond, which is compressed by as much as 14%. Therefore, while some substitution of Si atoms by Al may occur, we rule out as unlikely that Al would form an ordered underlayer in the $\sqrt{3}\times\sqrt{3}$ configuration in Si(111).

We list below the atomic displacements predicted by total-energy calculation (in parentheses)[10] and those obtained in the present LEED work for comparison. The notations introduced in Ref. 10 are used:

$$\delta r(2)=0.15\pm0.2\ \text{Å}\ (0.12\ \text{Å})\ ,$$

$$\delta z(2)=0.02\pm0.1\ \text{Å}\ (-0.02\ \text{Å})\ ,$$

$$\delta z(3\text{a})=0.44\pm0.1\ \text{Å}\ (0.33\ \text{Å})\ ,$$

$$\delta z(4\text{a})=0.32\pm0.15\ \text{Å}\ (0.17\ \text{Å})\ ,$$

$$\delta z(3\text{b})=0.16\pm0.1\ \text{Å}\ (0.11\ \text{Å})\ ,$$

$$\delta z(4\text{b})=0.08\pm0.15\ \text{Å}\ (0.09\ \text{Å})\ ,$$

$$d_{1\text{-}3\text{a}}=2.63\pm0.1\ \text{Å}\ (2.45\ \text{Å})\ .$$

Within quoted errors, the agreement is good. The only discrepancy of concern (by 0.18 Å) is the value of $d_{1\text{-}3\text{a}}$. One can view this distance as a measure of the strength of bonding between the Al adatom and the second-layer Si atom directly below. Both our result and that of Ref. 10 give the bond length between Al and its three first-layer Si neighbors as 2.49 Å. Our result indicates that the Al—Si (second-layer) bond is *much weaker* than the three Al—Si (first-layer) bonds, while the result of Ref. 10 suggests a reverse relationship. Since Al is a valence three element, our result presents a reasonable chemical picture.

In summary, we have carried out a quantitative dynamical LEED intensity analysis of a Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Al structure. We found that the Al atoms in a $\sqrt{3}\times\sqrt{3}$ array are absorbed on threefold-symmetrical sites above Si atoms in the second layer. The associated distortions of the substrate structure are indicated.

Three of us (W.S.Y., H.D.S., and F.J.) are grateful to the National Science Foundation for partial support of this work with Grant No. DMR-87-09021. Another (S.Y.T.) acknowledges the support of Office of Naval Research (ONR), U.S. Department of Defense, under Grant No. N00014-90-J-1749.

---

[*] Present address: Department of Physics, Peking University, Beijing 100 871, People's Republic of China.

[†] Present address: Department of Physics, University of Houston, Houston, Texas 77204-5504.

[1] J. J. Lander and J. Morrison, Surf. Sci. **2**, 553 (1964).

[2] M. Kelly, G. Margaritondo, J. Anderson, D. J. Frankel, and G. J. Lapeyre, J. Vac. Sci. Technol. A **4**, 1396 (1986).

[3] T. Kinoshita, S. Kono, and T. Sagawa, Phys. Rev. B **32**, 2714 (1985).

[4] T. Kinoshita, S. Kono, and T. Sagawa, Solid State Commun. **56**, 681 (1985).

[5] G. V. Hansson, R. Z. Bachrach, R. S. Bauer, and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981).

[6] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flodström, Phys. Rev. B **31**, 3805 (1985).

[7] J. M. Nicholls, B. Reihl, and J. E. Northrup, Phys. Rev. B **35**, 4137 (1987).

[8] R. J. Hamers and J. E. Dumuth, J. Vac. Sci. Technol. A **6**, 512 (1988).

[9] R. J. Hamers, Phys. Rev. B **40**, 1657 (1989).

[10] J. E. Northrup, Phys. Rev. Lett. **53**, 683 (1984).

[11] M. A. Van Hove and S. Y. Tong, *Surface Crystallography by LEED* (Springer-Verlag, Berlin, 1979).

[12] M. A. Van Hove, W. H. Weinberg, and C. H. Chan, *Low Energy Electron Diffraction* (Springer-Verlag, Berlin, 1986).

[13] H. Huang, S. Y. Tong, W. E. Packard, and M. B. Webb, Phys. Lett. **130A**, 166 (1988).

[14] S. Y. Tong, H. Huang, C. M. Wei, W. E. Packard, F. K. Men, G. Glander, and M. B. Webb, J. Vac. Sci. Technol. A **6**, 615 (1988).

[15] H. Huang, C. M. Wei, H. Li, B. P. Tonner, and S. Y. Tong, Phys. Rev. Lett. **62**, 559 (1989).

[16] W. C. Fan, A. Ignatiev, H. Huang, and S. Y. Tong, Phys. Rev. Lett. **62**, 1516 (1989).

[17] H. Huang, S. Y. Tong, J. Quinn, and F. Jona, Phys. Rev. B **41**, 3276 (1990).

[18] F. Jona, J. A. Strozier, Jr., and P. M. Marcus, in *The Structure of Surfaces*, edited by M. A. Van Hove and S. Y. Tong (Springer-Verlag, Berlin, 1985).

[19] W. Moritz, J. Phys. C **17**, 353 (1984).

[20] M. A. Van Hove, S. Y. Tong, and M. H. Elconin, Surf. Sci. **64**, 85 (1977).