Measurement of the Silicon (111) Surface Contraction

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Distinct differences have been found in the response of LVV and KLL Auger yields from 7×7 and 1×1 Si(111) surfaces probed with x-ray standing-wave excitations. If we take into account the shorter mean free path of the LVV electrons, the differences can be explained by a contraction of the top two (111) atom planes by approximately 0.5 Å. This agrees well with earlier analyses of ion-scattering measurements, but such a contraction has not been detected in other surface measurements or predicted by pseudopotential calculations. Current stacking-fault models of the 7×7 reconstruction may require modification in order to be consistent with these standing-wave measurements.

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The 7×7 reconstructed (111) surface of silicon is undoubtedly the most studied structure in surface physics today.[1] The actual geometrical arrangement of the surface atoms is not yet determined, however, and hence the Si(111) surface has become a challenge for every new experimental and theoretical structural probe. Models have been suggested by measurements made with low-energy electron diffraction (LEED),[2-4] ion-scattering spectroscopy,[5,6] scanning tunneling microscopy,[7,8] transmission electron diffraction,[9-11] and photoelectron spectroscopy,[12] among others; some of these models have been tested by total-energy pseudopotential calculations.[13,14] We report here x-ray standing-wave measurements of the 7×7 and 1×1 phases of the Si(111) surface, which reveal a significant contraction of the surface planes toward the bulk. This result is corroborated by earlier ion-scattering studies,[5] although the latter results have been reinterpreted as indicating a surface stacking fault instead of a contraction[4]; the stacking-fault models without contractions appear to be inconsistent with the standing-wave results.

The x-ray standing-wave technique is by now well established.[15,16] The position of an atom within a crystal unit cell is determined by the monitoring of a characteristic photon or electron emission yield as the x-ray standing wave excited at a Bragg reflection is scanned through the unit cell. This diffraction condition can be described as the result of a Bragg band gap in the spectrum of x-ray traveling-wave solutions of Maxwell's equations inside the crystal. Within the gap are standing-wave solutions, which are in effect the superposition of the incident and diffracted x-ray traveling waves. In the Bragg geometry only one standing-wave solution is excited, with nodal planes parallel to the crystal diffraction planes and with the same periodicity as these planes.[17] This standing wave is made to go from in phase to out of phase with the diffraction planes as the scattering wave vector is scanned through the Darwin region of total reflectivity. This modulates the local electric field intensity at each point within the unit cell, so that absorption and hence emission from atoms at particular sites become strong functions of the scattering wave vector. By the fitting of measured emission curves with a simple theoretical expression, locations within the unit cell of surface or impurity atoms have been determined to better than 1% of a lattice constant.[18-20]

Only recently have the practical difficulties of performing this measurement on a surface maintained in ultrahigh vacuum been overcome.[21,22] Briefly, the experimental configuration consists of a standard UHV chamber equipped with LEED, an electron spectrometer, and thin beryllium windows for the x-ray beam paths. Oriented Si(111) crystals were heated in vacuum until no surface contamination could be seen on the Auger-electron spectrum, and the desired Leed pattern, 7×7 (annealed surface) or 1×1 (quenched surface), was obtained. With use of the Cornell High Energy Synchrotron Source, a nondispersive Si(111) monochromator[23] produced a suitably collimated incident beam which diffracted from the specimen located at the focus of the electron spectrometer. This permitted the measurement of the Si LVV and KLL Auger electrons during standing-wave excitation.

During monitoring of a peak in the Auger spectrum, the electron spectrometer also sees a background due in part to inelastically scattered photoelectrons; these will not generally have the same standing-wave behavior as a result of x-ray extinction effects. Each Auger peak measurement was followed by an identical measurement at a slightly higher energy, to determine the appropriate background signal. The difference of these two data sets should then give the standing-wave behavior of the zero-loss Auger electrons.

Curves of this type are shown in Fig. 1 for the 90-eV *LVV* and 1610-eV *KLL* Auger electrons from a 7×7 reconstructed Si(111) surface. The clear difference between the *LVV* and *KLL* curves leads to the primary conclusion of this measurement, namely that the surface is significantly relaxed. This follows since the difference in standing-wave behavior can only be due to the different electron mean free paths, approximately 7 Å for the *LVV* and 25 Å for the *KLL*[24]; if there were no relaxation of the surface planes in the surface-normal direction, these two curves would be identical.[25]

Nearly identical results with the same clear difference in *LVV* and *KLL* behavior have also been recorded from a clean 1×1 surface and from a 1×1 surface contaminated with small amounts of carbon and oxygen. The similarity of the 7×7 and 1×1 structures has previously been inferred from ion scattering[6] and photoelectron spectroscopy.[12] All of the measured *KLL* curves, which sample a greater depth of the crystal, are very similar to the results which would be obtained from an ideal, unrelaxed Si(111) crystal. Thus the observed difference between the *LVV* and *KLL* curves can only be due to shifts of layers (in the surface-normal direction) localized near the surface, within a depth comparable to the *LVV* electron mean free path.

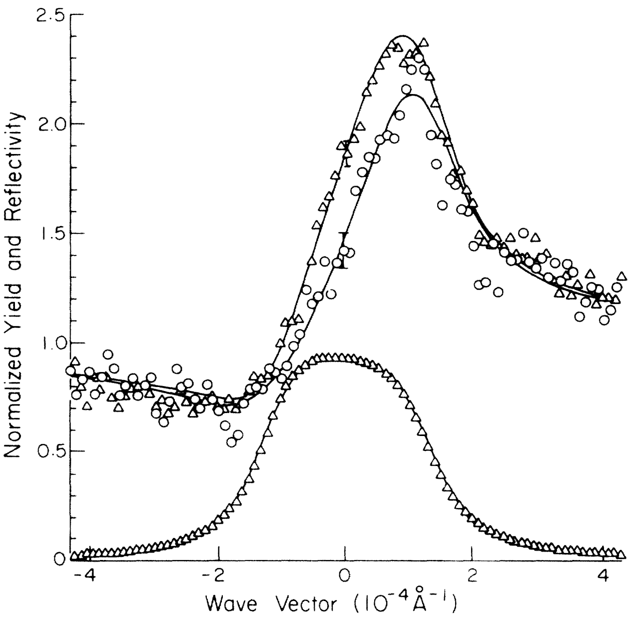

FIG. 1. Standing-wave yields from a 7×7 reconstructed Si(111) surface for (circles) the *LVV* and (triangles) *KLL* Auger peaks; solid lines were generated by the calculation described in the text. The error bars indicate the statistical uncertainties. The difference in these curves can be explained by a surface contraction of about 0.5 Å. The lowest curve shows the x-ray reflectivity data and a calculated fit.

To estimate the magnitudes and directions of these shifts, we have constructed a model of the specimen as a perfect semi-infinite crystal except for the top two atom planes, which are allowed to occupy any position in the surface-normal direction. This model of course cannot represent all the details of the physical 7×7 surface, since it only involves relaxations in the surface-normal direction. We then calculated the normalized Auger-electron yield Y as a function of scattering wave vector $\mathbf{K}$, using[26,27]

$$Y(\mathbf{K}) = \sum_{i=1}^{\infty} w_i \left[1 + \left| \frac{E_H}{E_0} \right|^2 + 2P \left| \frac{E_H}{E_0} \right| f_i \cos\left(\phi - \frac{2\pi \Delta d_i}{d_H} \right) \right], \tag{1}$$

from each configuration, i.e., set of positions $\{\Delta d_i\}$ relative to the diffraction planes, where i is the layer number (top layer corresponds to $i=1$). Y is equal to 1 when $\mathbf{K}$ is not in the vicinity of the reciprocal lattice vector $\mathbf{H}$ corresponding to the diffraction planes (of spacing $d_H = |\mathbf{H}|^{-1}$). E_0 and E_H are the incident and reflected electric fields, respectively, and ϕ is the standing-wave phase; the $\mathbf{K}$ dependence of Y is contained in $|E_H/E_0|$ and ϕ.[26,27] P is the x-ray polarization factor. For each layer, w_i is a weighting factor given by

$$w_i = \exp(-D_i/\lambda) / \sum_{i=1}^{\infty} \exp(-D_i/\lambda), \tag{2}$$

where D_i is the depth of layer i below the surface and λ is the Auger electron mean free path. f_i is the fraction of atoms within layer i occupying a position Δd_i (with the remaining fraction $1-f_i$ randomly distributed in the $\mathbf{H}$ direction). Atomic vibration effects were included in the analysis but, for clarity, are not explicitly shown in Eq. (1); the Debye-Waller factor for the Si(111) reflection at room temperature is ≈ 0.99. Extinction is ignored in Eq. (1), because the Si(111) extinction depth (a few microns) is much larger than the Auger electron mean free path (a few angstroms).

The yield Y calculated for each set of positions $\{\Delta d_i\}$ via Eq. (1) was convoluted with the monochromator transmission function and compared with the *LVV* data for a best fit with use of a least-squares technique. The calculations assumed perfect planes, and hence the f_i's in Eq. (1) were set equal to 1.

The results of this variational calculation are shown in Table I. If we assume a 7-Å mean free path, the average shift of the top pair of (111) atom planes is a contraction by (18 ± 5)% of the (111) lattice constant, or about 0.5 Å. This is in very good agreement with the estimated shift of 0.4–0.6 Å found in the initial in-

TABLE I. The positions of the top two Si(111) atom layers derived from the measured standing-wave yields are given for three different surfaces: clean 7×7, clean 1×1, and a 1×1 surface contaminated with small amounts of carbon and oxygen. The positions were derived with use of three different values of the *LVV* electron mean free path: 5, 7, and 9 Å. They are given in units of the (111) spacing (3.14 Å) outward from the underlying (111) diffraction plane (i.e., from the midplane of the third and fourth layers). The bulk or reconstructed positions are 1.125/0.875, the first value referring to the top layer and the second one to the second layer.

Surface	Mean free path (Å)		
	5	7	9
Clean 7×7	0.99/0.72	0.94/0.70	0.88/0.71
Clean 1×1	0.98/0.72	0.93/0.71	0.87/0.72
Contaminated 1×1	0.94/0.74	0.84/0.78	0.80/0.80

terpretation of the ion-scattering work of Culbertson, Feldman, and Silverman.[5] (The ion scattering, however, could not distinguish between a contraction and an expansion of this magnitude.) Figure 2(a) illustrates how the Si(111) surface would appear with a uniform contraction of this amount. Figure 2(b) shows a second model which is consistent with our data, in which the second layer is in the ideal crystal position while the top layer is shifted into the bulk by about 1.0 Å. The displacements in Fig. 2(b) leave the number of first nearest neighbors unchanged but significantly distort bond angles; the energetics of this type of reconstruction do not seem to have been considered.

One of the early models of the 7×7 reconstructed Si(111) surface involves a partial layer of adatoms above the topmost complete double layer.[28] This model is in fact supported by recent tunneling microscopy observations.[7] We have calculated the effect on the Auger yields from the adatoms at the suggested density of 12 per 7×7 surface unit cell,[7] and conclude that such a partial layer does not affect our result for the surface double-layer contraction to within the quoted uncertainty.

Contractions of the magnitude observed here have not been found from analyses of other experiments or from pseudopotential calculations.[13,14] Because our result is apparently anomalous, we review here some of the important assumptions in this analysis. Firstly, we should emphasize that in modeling the contribution to the observed Auger signal we have used the conventional procedure of estimating the attenuation via an exponential function involving an average mean free path; this may not be completely satisfactory because of the lateral variations in valence-electron density across the Si reconstructed surface layer. It would also be highly desirable to have measurements of Auger yields as functions of angle of emission with respect to the surface normal; such data would allow a determination of the distribution of layer relaxations with depth. All of the Auger data had subtracted from them a background signal which was measured at a slightly different energy. We did not attempt to model the energy dependence of the background; instead, we simply assumed it was constant. We found that artificially suppressing or enhancing the background by up to 100% could not remove the distinct difference in the *LVV* and *KLL* curves. Finally, the calculations assumed perfect planes, neglecting distortions which might occur at step edges and other defects. We assume from the quality of the LEED patterns that these distortions only affect a negligible fraction of the surface area.

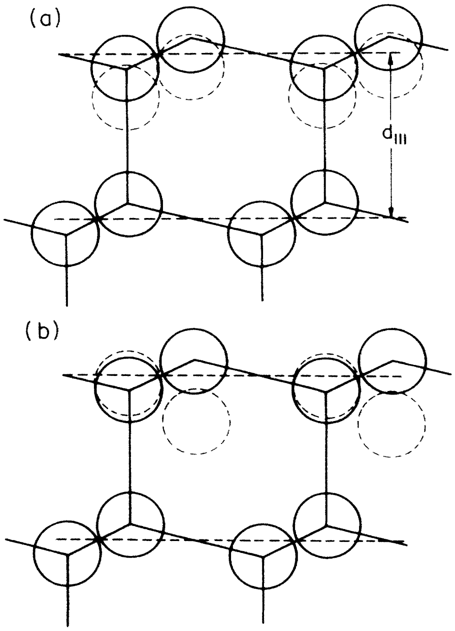

FIG. 2. (a) A cross section of the Si(111) surface for an unreconstructed surface (solid circles) and a surface with the top two layers uniformly contracted by about 0.5 Å, of 18% of the (111) spacing. (b) The same net contraction with the second layer remaining near the bulk position while the top layer is contracted by twice the average amount. These two configurations cannot be distinguished by standing-wave measurements made only in the [111] direction.

It is difficult to find a model of the surface which includes this contraction without large changes in bond lengths or angles. In stacking-fault models there is a large shift of atom positions within the (111) planes but no change in the surface-normal direction. Such stacking faults would be completely undetectable in this standing-wave measurement, since the standing-wave modulation is only in the [111] direction. Because of this, our results cannot confirm nor rule out the presence of surface-stacking faults which may be involved in producing the observed 7×7 superlattice. However, any such model of the Si(111) surface would require inclusion of a net displacement of the topmost layers toward the bulk in order to be consistent with the standing-wave measurement.

In closing, we would like to stress that the conclusion from the standing-wave data that the surface is contracted relies on a relatively straightforward analysis. The standing-wave determination of positions in the direction normal to the surface should serve as an ideal complement to scanning-tunneling-microscopy topographs in elucidating the true surface structure. It will also be interesting to undertake further studies of surface contraction on other orientations and other materials with different electronic bonding configurations.

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