Surface Phase Separation of Vicinal Si(111)

R. J. Phaneuf and Ellen D. Williams
Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742
(Received 29 December 1986)

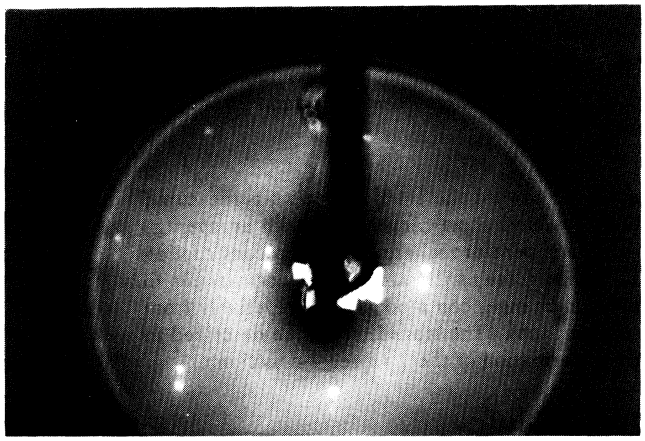
The structure of a vicinal Si(111) surface, misoriented by 6° toward the [1$\bar{1}$0] direction, is measured as a function of temperature. At $T \gtrsim 810$ °C the surface steps have short-range order with an average step-step spacing of 28.4 ± 1.6 Å. Upon cooling through the temperature where the 7×7 reconstruction appears, the spacing begins to decrease although the step height remains the same. This corresponds to clustering of the steps to form a new face whose misorientation changes continuously and reversibly from $6.3° \pm 0.4°$ at high temperature to $17.0° \pm 3.0°$ at low temperature. The transition can be described in terms of changes in the equilibrium crystal shape induced by formation of the 7×7 reconstruction.

PACS numbers: 68.35.Bs, 61.14.Hg, 68.35.Rh

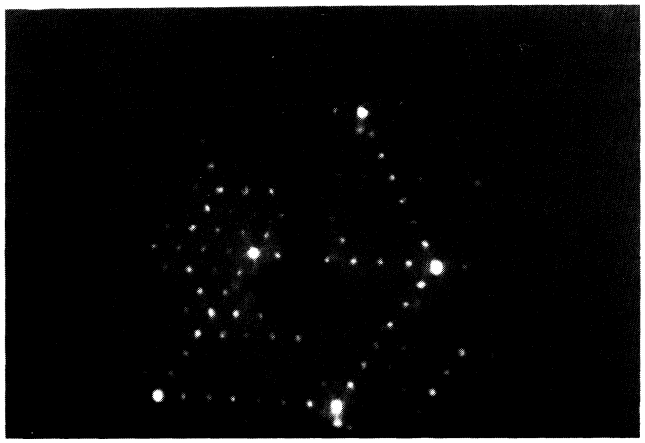
By cutting a crystal a few degrees away from a low-index orientation, it is possible to create a surface which does not correspond to one of the equilibrium faces of the crystal. The behavior and structure of such vicinal surfaces is clearly related to theories of equilibrium crystal shape and of surface roughening transitions.[1-6] However, while there has been a large amount of experimental work on vicinal surfaces,[7] the results, in general, have not been interpreted in terms of crystal shape. This may be because, somewhat surprisingly, clean vicinal surfaces show little tendency to break up into large facets of low-index orientation. Most commonly, the surfaces display terraces of the nearby low-index plane separated by steps which are a small number of atomic layers high. Vicinal surfaces are thus often also referred to as stepped surfaces. There have been a number of reports of transitions involving the step configuration on vicinal surfaces. In most cases, such transitions occur as a result of the addition of some impurity to the surface, and are only reversible if the impurity can be removed.[8-10] However, in a few cases, fully reversible step transitions have been observed on clean surfaces.[11-13] Such transitions are of intrinsic interest,[6] and may also be important because of the light that they shed on the interatomic forces at surfaces.

In this paper, we report measurements of reversible changes in surface step structure, which for the first time can be quantitatively related to theories of the equilibrium crystal shape. The first description of this transition has been reported elsewhere.[14] The experiments were performed on a Si surface cut away from the (111) plane by 6° toward an azimuth within a few degrees of the [1$\bar{1}$0] direction. The samples were cleaned by heating in a vacuum (2×10^{-10} Torr) to 1250 °C. No impurity peaks were observable in the Auger-electron spectrum following this treatment. Sample temperature was monitored by a W-5%-Re/W-26%-Re thermocouple clamped near the edge of the sample. The thermocouple was calibrated at high temperature against a disappearing filament pyrometer. The surface structure was measured by low-energy electron diffraction (LEED) with use of a commercial four-grid optics. Measurements of the diffraction beam profiles were made by imaging the diffraction pattern onto a silicon-intensified vidicon screen. Scans of the intensity along chosen directions of the pattern were performed with an aperture for which the width perpendicular to the direction of scan was chosen to be a few times the apparent full width at half maximum of the feature being scanned.

The diffraction patterns observed at $T > 810$ °C and at 200 °C are shown in Fig. 1. At high temperature the surface shows a (1×1) LEED pattern, with energy-dependent splitting of the diffraction beams due to the step structure. Analysis of the energy dependence and size[15,16] of the splitting measured for seven different diffraction beams shows that at high temperature, the surface contains steps of height 3.12 ± 0.07 Å and separation 28.4 ± 1.6 Å, consistent with the 6° angle of cut.[17] A broadening of the split beams at the out-of-phase conditions indicates that the step-separation distribution contains some disorder.[18] The direction of the splitting shows that the step edges run parallel to the [1$\bar{1}$2], in agreement with the direction of misorientation. Well below the transition temperature, the characteristic (7×7)-Si(111) LEED pattern with unsplit integer-order beams is observed. The high-temperature split beams have increased in separation to form weak satellites around the integer-order beams. These satellites change in position with respect to the integer-order beams with the same dependence on energy as at high temperature. The transition between the two LEED patterns occurs in the temperature range 500–810 °C, similar to the observation for a sample with 4° misorientation.[14] Scans of the intensity distribution along the direction of beam splitting through the transition region are shown in Fig. 2. At high temperature, the splitting shown in Fig. 1(a) is clearly visible. As the temperature decreases below 810 °C, an intensity component at the integer-order position begins to appear. Simultaneously, the split beams begin to move apart and decrease in intensity. The beams of the 7×7 pattern appear at the same temperature as the unsplit beams and increase in intensity over



(a)



(b)

FIG. 1. LEED patterns above and below the transition region. (a) $T=910\,^{\circ}C$, incident energy $=47$ eV, incident angle $=8^{\circ}$. (b) $T=170\,^{\circ}C$, incident energy $=34$ eV, incident angle $=8^{\circ}$.

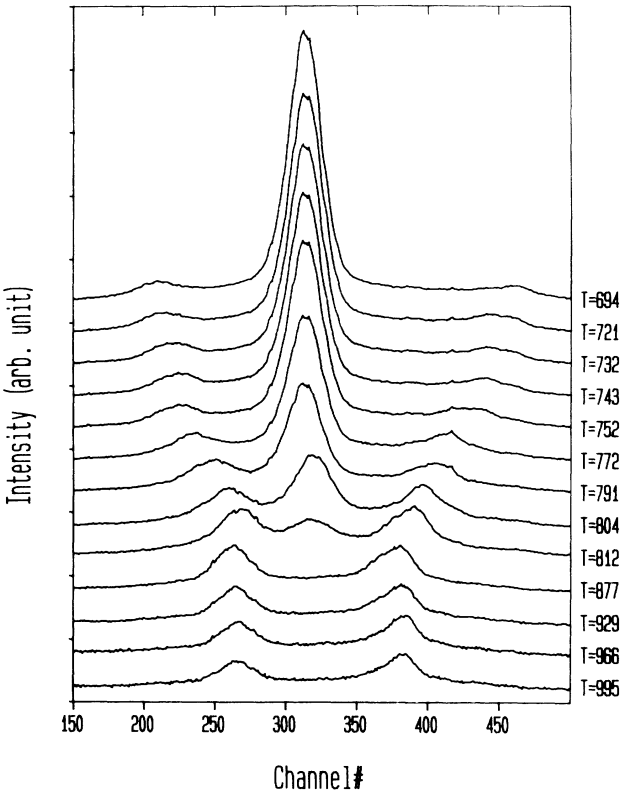


FIG. 2. Angular profiles of the specular beam in the direction of splitting as a function of temperature. Incident energy $=47$ eV, incident angle $=8^{\circ}$. At this energy, 141 channel numbers $=|a^*|/7$, where a^* is the first-order reciprocal-lattice vector of the (111) surface. The asymmetry of the split beams around the specular beam occurs because the incident energy is slightly less than the energy for out-of-phase scattering.

the same temperature range.[19] The temperature dependence of the various features is shown in Figs. 3 and 4.

To characterize the low-temperature step structure, the energy dependence of the positions of the split beams around four different integer-order beams was measured. The energy difference between in-phase conditions, when one of the split beams is at the same position as the integer-order beam, is directly related to the step height.[15,16] The energy dependence for all the measured beams corresponds to steps of 3.17 ± 0.10-Å height. Thus the step height has not changed through the transition region, although the increased splitting indicates a smaller separation between the steps. As a result of the low intensity of the satellite beams at the out-of-phase conditions, the value of the splitting was determined by fitting the observed energy dependence of the satellite positions. The best overall fit with the form $\Delta S_{\parallel}=\Delta S_{\perp}\tan\alpha$ gave values of from $0.27|a^*|$ to $0.38|a^*|$ for the splitting of the satellite beams around different integer-order beams. The spot splitting at low temperature thus corresponds to an average step-step separation of 10.4 ± 1.7 Å, compared to the separation of 28.4 ± 1.6 Å at high temperature. The value of 10.4 ± 1.7 Å is somewhat smaller than the value previously measured for a 4°-misoriented sample.[14]

These results indicate that through the transition, the steps move closer together forming clusters of steps. The step clusters are separated by large terraces of (111) orientation which give rise to the unsplit integer-order beams as well as the 7×7 pattern. The step clusters can be described as forming small surface regions more steeply inclined with respect to the (111) than the original angle of cut. The angle of orientation of these stepped parts of the surface with respect to the (111) is shown on the right-hand axis of Fig. 3. The size and spacing of these clusters could not be determined because of the limited resolution of the instrument. This

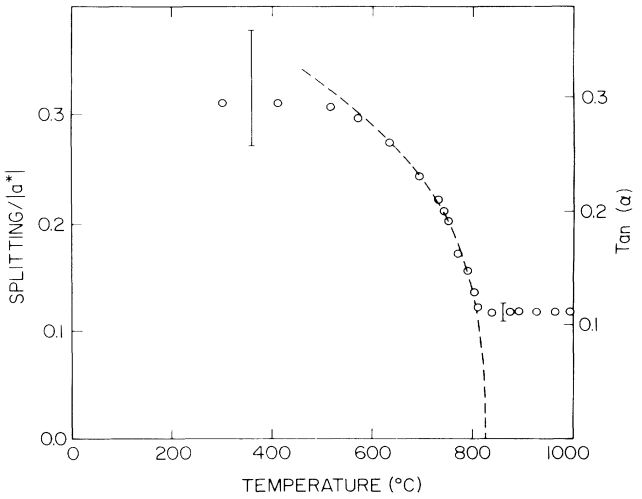


FIG. 3. Separation of the split beams around the specular beam as a function of temperature. Incident energy = 47 eV, incident angle = 8°. As described in the text, the step clusters form high-index surfaces misoriented by an angle α with respect to the (111). The misorientation corresponding to the observed splitting is shown on the right-hand axis. The error bars indicate the standard deviation in the absolute value of the orientation calculated from measurements of several different beams. The dashed line shows a preliminary fit of the data with a $t^{(\theta-1)/\theta}$ dependence, where t is the reduced temperature, $T_c = 826\,^{\circ}\mathrm{C}$ and $\theta = \frac{1}{3}$.

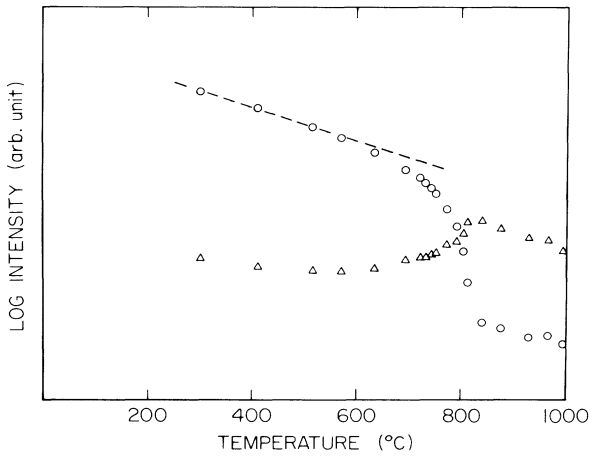


FIG. 4. Logarithm of the intensity of the specular beam (circles) and corresponding split beams (triangles) as a function of temperature. Energy and angle as in Fig. 3. The dashed line shows the Debye-Waller decrease in intensity well below the transition.

step rearrangement is dramatically different from the results reported for Si(111) misoriented in the $[2\bar{1}\bar{1}]$ and the $[\bar{2}11]$ directions.[11,13] The transitions occur in the same temperature range, and coincide with the "1×1" to 7×7 transition in all three cases. However, with decreasing temperature the step height and separation have been reported to double for the $[\bar{2}11]$ misorientation and triple for the $[2\bar{1}\bar{1}]$ misorientation.[11,13] The formation of a structure with the step separation determined by some intrinsic properties, rather than simply by the angle of misorientation, seems to be unique to misorientation towards the $[1\bar{1}0]$.

The step rearrangement described above is qualitatively expected from general thermodynamical considerations. Widely spaced steps are to be expected at high temperature due to the entropy gained by step-edge wandering. This is in agreement with our observation of step disorder at high temperature. At low temperature, energetic considerations may favor coalescence of the steps. In the case of Si(111), these simple ideas are complicated by the "1×1" to 7×7 transition which occurs in the temperature range of the step transitions. Reflection electron[20] and scanning tunneling[21] microscopic measurements have shown a strong correlation between the 7×7 structure and step edges. The experimental observations leave open the question of the mechanism by which the formation of the 7×7 reconstruction and the changes in the step structure simultaneously occur. Possible microscopic models for the step rearrangement are discussed elsewhere.[14]

The observed step rearrangement appears to be a phase separation between the (111) surface and a high-index surface. This can be described in terms of the development of a sharp edge in the equilibrium crystal shape.[22,23] To explain the data, we hypothesize that at high temperature, the 6° misorientation corresponds to an orientation on the "rounded" or roughened surface. Upon cooling through the temperature for formation of a sharp edge in the crystal shape, this orientation no longer corresponds to a surface on the equilibrium crystal shape. The surface thus separates into the two closest allowed orientations, the (111) and the orientation just beyond the edge. With cooling, the orientation at the sharp edge shifts farther away from the (111). The orientation observed at the lowest temperature has a measured step-step separation of 10.4 ± 1.7 Å, which encompasses terrace configurations containing 2.5 (9.6 Å) or 3 (11.5 Å) Si(111) unit cells. The surface orientations corresponding to these configuration are (735) and (423), respectively. This low-temperature orientation may represent an equilibrium crystal face, or it may be a metastable surface trapped because Si surface diffusion is extremely slow below 500 °C.

The correlation between the "1×1" $\rightleftharpoons$ 7×7 transition and the temperature at which the sharp edge appears can be discussed in analogy with the effect of surface impurities, which can change the equilibrium crystal shape.[23] At some temperature, the free-energy curves corresponding to the metastable shapes with and without the reconstruction (impurity) may cross, causing the formation of

a sharp corner in the crystal shape simultaneously with the onset of the reconstructive transition. This picture suggests that as the cut angle decreases, the temperature at which phase coexistence begins will approach the temperature of the "1×1" to 7×7 transition on the flat (111) surface. Further work is in progress to quantify this description by measurement of the transition over a range of misorientations.

In the above description, the orientation of the sharp edge should follow the shape of the metastable crystal without the 7×7 reconstruction. For the assumed rounded crystal shape, all orientations α are allowed and near the transition one expects $\tan\alpha \sim z^{(\theta-1)/\theta}$, where z is the distance perpendicular to the (111) facet. One then expects the free energies associated with the two metastable surfaces to change analytically in $t=(T-T_c)/T_c$, so that $z \sim t$ for small t. A preliminary fit of the data with the form $\tan\alpha \sim t^{(\theta-1)/\theta}$ is shown in Fig. 3. The fit shown was forced to a value of $\theta=\frac{1}{3}$. However, by varying the data range of the fit, the value of the exponent can be changed to $\theta=\frac{1}{2}$. Thus the fit is consistent with both the prediction of a Pokrovsky-Talapov exponent of $\theta=\frac{3}{2}$,[22,24] and with the mean-field prediction of $\theta=2$, which could be appropriate if the interaction between steps is of sufficiently long range.[25,26]

We gratefully acknowledge many useful discussions with N. C. Bartelt, T. L. Einstein, G. Akinci, and T. Ohno, and thank R. Hwang for the curve fitting and C. Rottman for a critical reading of the manuscript. This work has been supported by the U.S. Department of Defense, by IBM, and by the National Science Foundation under Grant No. DMR-85-04163.

[1]W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. Roy. Soc. London **243**, 299 (1951).

[2]E. E. Gruber and W. W. Mullins, J. Phys. Chem. Solids **28**, 875 (1967).

[3]C. Jayaprakash, C. Rottman, and W. F. Saam, Phys. Rev. B **30**, 6549 (1984).

[4]T. Burkhardt and P. Schlottmann, Z. Phys. B **54**, 151 (1984).

[5]S. T. Chui and J. D. Weeks, Phys. Rev. B **23**, 2438 (1981).

[6]A. Saxena, T. Ala-Nissilä, and J. D. Gunton, Surf. Sci. **169**, L231 (1986).

[7]M. A. Van Hove and G. A. Somorjai, Surf. Sci. **92**, 489 (1980), and references therein.

[8]G. Comsa, G. Mechtersheimer, and B. Poelsema, Surf. Sci. **119**, 159 (1982).

[9]H. V. Thapliyal and J. M. Blakeley, J. Vac. Sci. Technol. **15**, 600 (1978).

[10]T. Jach and J. C. Hamilton, Phys. Rev. B **26**, 3766 (1982).

[11]B. Z. Olshanetsky and A. A. Shklyaev, Surf. Sci. **82**, 445 (1979).

[12]B. Z. Olshanetsky, V. I. Mashanov, and A. I. Nikiforov, Surf. Sci. **111**, 429 (1981).

[13]V. I. Mashanov and B. Z. Olshanetskii, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 290 (1982) [JETP Lett. **36**, 355 (1982)].

[14]G. Akinci, T. Ohno, and E. D. Williams, Phys. Rev. B (to be published).

[15]W. P. Ellis and R. L. Schwoebel, Surf. Sci. **11**, 82 (1968).

[16]M. Henzler, Surf. Sci. **22**, 12 (1970).

[17]R. J. Phaneuf and E. D. Williams, Phys. Rev. B **35**, 4155 (1987).

[18]P. R. Pukite, C. S. Lent, and P. I. Cohen, Surf. Sci. **161**, 39 (1985).

[19]The "1×1" to 7×7 transition temperature previously measured on a nominally unstepped surfaced by P. A. Bennett and M. B. Webb, Surf. Sci. **104**, 74 (1981) is 867 °C. It is difficult to compare this value directly with our value because of calibration uncertainties for different pyrometers.

[20]N. Osakabe, Y. Tanishiro, K. Yagi, and G. Honjo, Surf. Sci. **109**, 353 (1981).

[21]R. S. Becker, J. A. Golovchenko, E. G. McRae, and B. S. Swartzentruber, Phys. Rev. Lett. **55**, 2028 (1985).

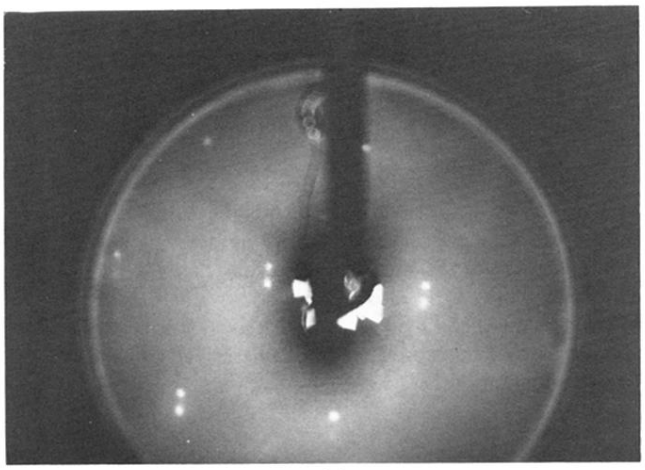
[22]C. Rottman and M. Wortis, Phys. Rep. **103**, 59 (1984).

[23]J. W. Cahn, J. Phys. (Paris), Colloq. **12**, C6-199 (1982).

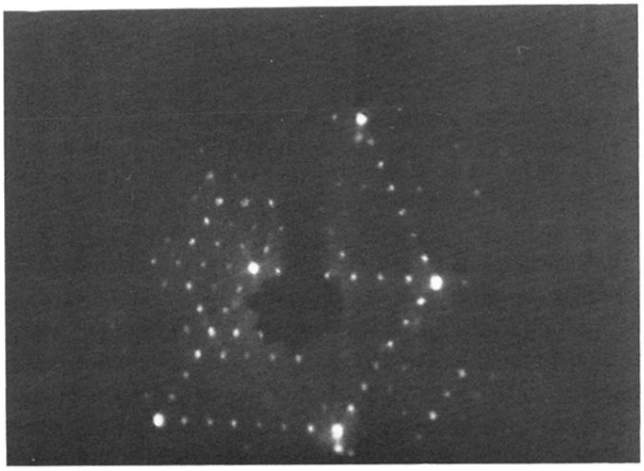
[24]C. Rottmann, M. Wortis, J. C. Heyrand, and J. J. Metois, Phys. Rev. Lett. **52**, 1009 (1984).

[25]J. J. Saenz and N. Garcia, Surf. Sci. **155**, 24 (1985).

[26]J. J. Metois and J. C. Heyrand, Surf. Sci. **180**, 647 (1987).



(a)



(b)

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