Step-Height Mixtures on Vicinal Si(111) Surfaces

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Scanning tunneling microscopy (STM) and high resolution low-energy electron diffraction measurements on vicinal (stepped) Si(111) surfaces reveal mixtures of single- and triple-layer-height steps, with the density of triples increasing with total step density. The diffraction signature of the step mixtures is an incommensurate spacing; however, the STM data show no periodic sequence of singles and triples. Instead, there is a random sequence with specific ratios of the lengths of terraces bounded by steps of different heights, quantitatively consistent with the energetic ground state for elastically interacting steps.

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The nature of steps on surfaces determines the morphology of surfaces under both equilibrium and nonequilibrium conditions [1]. One aspect of step behavior, which has been the subject of extensive discussion, is that of the formation of mixtures of steps of different height [2–7]. The possibility of such mixtures arises when the formation energy of a multilayer-height step from single-layer-height steps is comparable to the energetic interactions between steps. In this case one qualitatively expects that multilayer-height steps will be favored at large step densities (i.e., at large vicinal angles), while single-layer-height steps will be favored at elevated temperatures. Depending on the nature of the step-step interactions, the two step heights can coexist either in two distinct phases [5,8] or as a uniform mixture [4]. Observations of step mixtures thus provide information about the energetics of step formation and step interactions.

Surface strain is expected to lead to a significant elastic repulsion between steps [9,10], and evidence for such an interaction has been reported experimentally [10–12]. The theoretical expectation is that a mixture of step heights with elastic interactions will not phase separate. The ground-state configuration is, in fact, predicted to consist of a periodic array of mixed heights (e.g., *ssstssstssst*...) which follows a devil's staircase progression with increasing step density [4]. In a devil's staircase progression [13] only rational numbers are allowed for the ratio of single- to multiple-height steps. When entropy is important, this rigorous periodicity will be relaxed to allow a distribution of spacings between the multilayer steps (e.g., *sstssssstssst*...). In this case the average periodicity of the structure need not be commensurate with the original step-step spacing [13]. The extreme alternative to the periodicity of a devil's staircase or incommensurate sequence would be a totally random mixture. In this case, long-range order of the step structure would be lost [14].

Scanning tunneling microscopy (STM) provides a new and direct capability of measuring structural distributions for comparison with theoretical predictions. We have experimentally investigated step-height mixtures as a function of step density on vicinal Si(111) surfaces using both high resolution electron diffraction [15] and STM [11]. Previous results have shown that these surfaces contain a mixture of single- and triple-layer-height steps [16]. The single-height steps interact repulsively with a strength that falls off as the inverse square of the step-step separation [11,12]. Here we address the question of how this interaction determines the sequence and terrace length distribution of steps in a step-height mixture. The samples used in this study were commercially obtained Si wafers nominally inclined by 1.3°, 2.5°, 3.8°, and 6° towards the high symmetry $[\bar{1}\bar{1}2]$ direction. The samples were cleaned by a procedure described previously [16,17].

The high resolution low-energy electron diffraction (HRLEED) measurements show that a change in step height occurs simultaneously with the formation of the (7×7) reconstruction at approximately 860 °C [16,18]. Figure 1 shows the temperature dependence of the (0,0) beam profiles at an out-of-phase condition for different angles of misorientation. Inspection of the ratio between the splitting above and below the (7×7) reconstruction temperature T_c shows that the ratio is a function of angle, varying from about $\frac{1}{3}$ at 6° to 0.69 at 2.5° and almost 1.0 at 1.3° of miscut. The structure of the steps was further clarified by measurement of the energy dependence of the diffraction profiles, as illustrated in Fig. 2 for the 4.0° misoriented sample. The results show that the low-T diffraction rods pass through an in-phase condition at nonintegral values of perpendicular momentum transfer. The beams corresponding to the original step periodicity are visible away from the out-of-phase conditions and become strong and sharp at the in-phase conditions. Furthermore, the slopes of the rods are identical, indicating that there has been no change in orientation, and thus no phase separation.

The traditional interpretation of the LEED observation of sharp beams at positions shifted from the $\frac{1}{3}$ position expected for a pure step-tripling transition would be that there is an incommensurate periodicity of the triple-single mixture. The veracity of the interpretation can be checked by direct observation of the step sequence using STM. A STM image which shows both single- and triple-layer height steps is presented in Fig. 3(a). Large-area profiles of the type depicted in Fig. 3(b) allow us to quantify the nature of the mixture of singles and triples

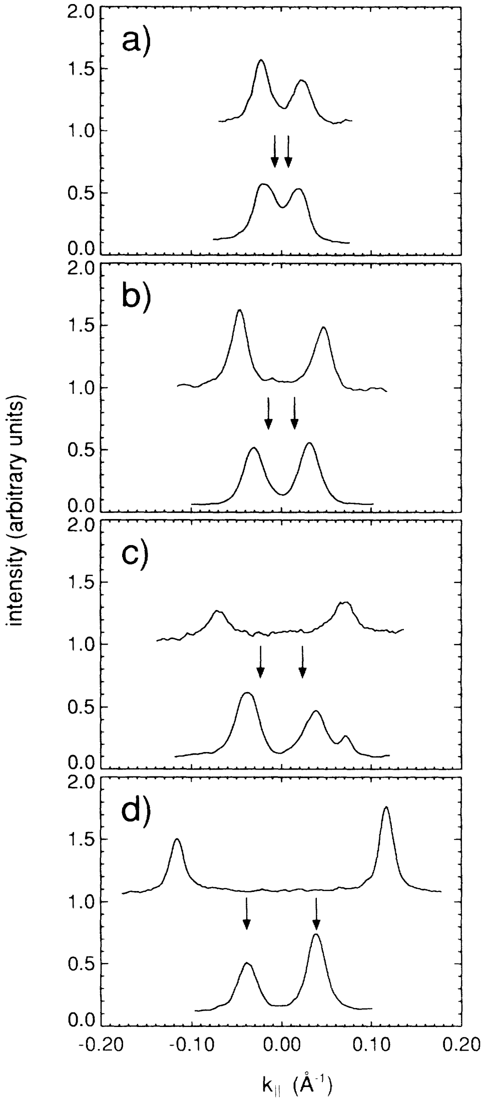

FIG. 1. The temperature dependence of (0,0) beam profiles at an out-of-phase condition for both single- and triple-layer-height steps for four misorientation angles: (a) 1.3°, (b) 2.5°, (c) 4.0°, and (d) 6.6°. For each miscut angle, the upper profile shows the beam splitting above the (7×7) reconstruction where the surface contains only single-layer-height steps and the lower one shows the incommensurate splitting at low temperature. The two arrows indicate the expected split beam positions if the surface contained a uniform array of triple-layer-height steps.

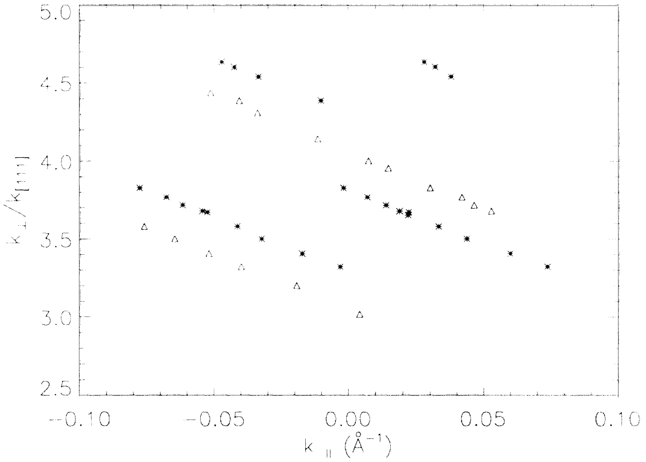

FIG. 2. The plot of $k_{\perp}$ vs $k_{\parallel}$ for a surface nominally misoriented 4.0° towards $[\bar{1}\bar{1}2]$ at room temperature. The horizontal coordinate is the component of the momentum transfer projected in the (111) plane. The vertical coordinate is the component of the momentum transfer perpendicular to the (111) plane. $k_{\perp}$ is expressed in the units of $k_{[111]}=2\pi/d_{[111]}$. Integral values of $k_{\perp}$ correspond to an in-phase condition for single-layer-height steps, half-integral values to an out-of-phase condition. Δ's denote the peak positions for the beams corresponding to the original step periodicity and $*$'s denote the beams associated with the incommensurate splitting.

on the surfaces. Inspection of this sequence immediately shows no evidence of a periodic sequence of singles and triples, as would be expected from theory [4] and from the observed incommensurate LEED spacing [13]. A quantitative analysis of the probability of observing n singles between a pair of triples confirms this observation: The distribution decays smoothly with no preferred spacings. Although there is no periodicity in the sequence of step heights, there is a nonrandom distribution of the values of the spacings shown in Table I. The results clearly show that multilayer-height steps bound significantly wider terraces than single-layer-height steps. This indicates that the step-step repulsion depends on the heights of the steps. The consistency of the HRLEED and STM results was checked by calculating the diffraction profiles from the Fourier transform of the STM

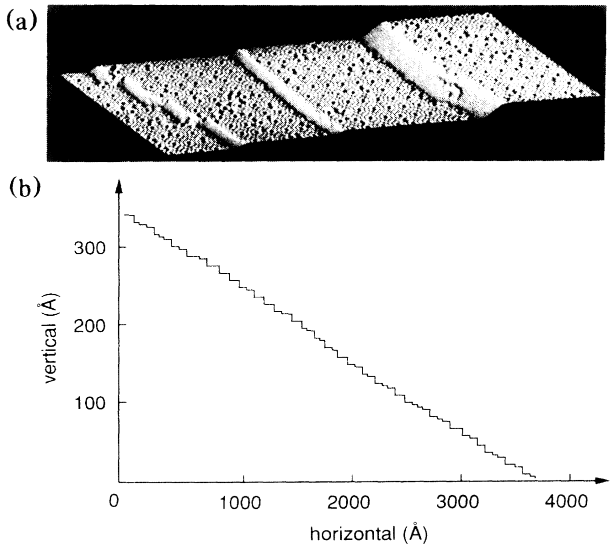

FIG. 3. (a) A STM scan from a 1.2° sample showing a triple-layer step and two single-layer steps on the surface. The area of the scan is 200 Å×800 Å. (b) A composite surface profile of a slowly cooled 5.1° misoriented surface.

TABLE I. STM measurements of the average lengths of terraces between two single-layer steps l_{ss}, two triple-layer steps l_{tt}, and a triple- and a single-layer step l_{st} as a function of misorientation angle. Misorientation angles are measured from the STM data. N_{tot} gives the total number of terraces observed in the large area STM scans. Because the terrace lengths are quantized to the (7×7) cell [26], the lengths in the table are in units of half the unit cell width or 23.3 Å.

Φ (deg)	N_{tot}	l_{tt}	l_{st}	l_{ss}	l_{tt}/l_{st}	l_{st}/l_{ss}
1.3 ± 0.1	622	⋯	9.2 ± 1.6	6.9 ± 0.9	⋯	1.33 ± 0.29
2.7 ± 0.3	1238	⋯	4.1 ± 0.4	3.3 ± 0.3	⋯	1.22 ± 0.17
5.2 ± 0.4	597	3.4 ± 0.2	2.9 ± 0.1	2.1 ± 0.1	1.18 ± 0.08	1.33 ± 0.10
6.4 ± 0.6	395	2.9 ± 0.3	2.4 ± 0.2	⋯	1.18 ± 0.13	⋯

data. The agreement with Figs. 1 and 2 is excellent [19].

The results can be understood by using elasticity theory to predict the behavior of step-height mixtures. In elasticity theory [20,21], a step "a" will interact with a neighboring step "b" with an energy given by $U_{ab} = C\tau_a\tau_b/l_{ab}^2$, where l_{ab} is the separation of the steps, τ_a and τ_b are the torques [22] of the steps created by strain fields associated with each step, and C is a material-dependent constant. This relation has been shown [6,21,23,24] to be a good approximation even when l_{ab} is on the order of a few lattice constants. The Hamiltonian for an array of interacting steps can thus be written as

$$H = C\sum_i \tau_i\tau_{i+1}/l_{i,i+1}^2 , \tag{1}$$

where $l_{i,i+1}$ is the step separation between step i and step $i+1$. In writing this equation we have neglected interactions across steps, as a first approximation.

To compare the theory with our data, we first obtain the ground-state structure for a given ratio of single- and triple-layer steps by minimizing H with respect to step separation l (terrace lengths) with the constraint of fixed misorientation angle. This minimization yields a striking prediction for ratios of terrace lengths:

$$\frac{l_{tt}}{l_{st}} = \frac{l_{st}}{l_{ss}} = \left(\frac{\tau_t}{\tau_s}\right)^{1/3} , \tag{2}$$

where l_{st}, l_{tt}, and l_{ss} are single-triple, triple-triple, and single-single terrace lengths, and τ_s and τ_t are the torques for single- and triple-layer steps, respectively. If surface stress were the only contribution to the torques at the step edges, then this ratio would be *precisely* the ratio of the step heights, which is 3 [20,21]. Given the further plausible assumption that the forces on the (unrelaxed) atoms at the step edges are independent of step height, this approximation should be good [23]. In fact, a comparison with the data presented in Table I shows that the measured terrace-length ratios come very close to the predicted value of $3^{1/3} \approx 1.44$.

The remaining question is why a random sequence of single and triple steps gives sharp beams with the observed incommensurate splitting in the diffraction pattern. Our analysis of Eq. (1), in which we have truncated the elastic interactions at nearest-neighbor distances, results only in the requirement that the sequence of steps contains no triple-triple pairs at triple densities less than one-half. Diffraction profiles calculated from Fourier transform of such sequences, given the terrace-length ratios of Eq. (2), agree very well with the observations of Figs. 1 and 2 [19], despite the randomness in the step sequence.

One can understand the incommensurability of the diffraction peaks by considering a surface in which all of the terrace lengths are equal, but the sequence of single- and triple-layer-height steps is random. At the out-of-phase condition for single-layer steps, the diffraction profile will be completely insensitive to the difference between single- and triple-layer steps. In this case the step sequence appears perfectly periodic so that the diffraction pattern will consist of pairs of (δ-function-like) split beams with separation $2\pi/l$, where l is the uniform terrace length. If we define the incommensurability Δ as the fractional displacement of the split beams from the ex-

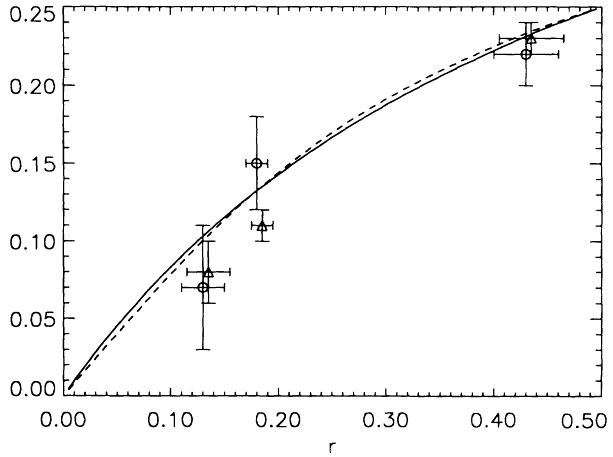

FIG. 4. The dependence of the incommensurability Δ on r, the fraction of steps which are triple-layer height for the models discussed in the text (solid line, $l_{st}/l_{ss} = 1$; dashed line, $l_{st}/l_{ss} = 1.44$), and from our HRLEED measurements (open circles) and STM measurements (triangles). The STM data are slightly shifted horizontally for clarity.

TABLE II. The number of single- and triple-height steps measured with STM were used to determine the fraction of triples r = number of triples/(number of triples plus number of singles). The relative spacing of the "satellite" beams, Δ, calculated by using the STM images and measured directly with diffraction are shown.

Φ (deg)	N'	M	N_{ss}	N_{st}	N_{tt}	r	Δ (STM)	Δ (LEED)
1.3 ± 0.1	544	78	516	106	···	0.13 ± 0.02	0.08 ± 0.02	0.07 ± 0.04
2.7 ± 0.3	1016	222	857	381	···	0.18 ± 0.01	0.11 ± 0.01	0.15 ± 0.03
5.2 ± 0.4	340	257	199	240	129	0.43 ± 0.03	0.23 ± 0.01	0.22 ± 0.02
6.4 ± 0.6	113	282	29	195	271	0.71 ± 0.06	0.27 ± 0.01	0.34 ± 0.04

pected position, $2\pi/b$, when the surface is completely covered by single-layer-height steps, then the dependence of the terrace length l on the fraction of triple-layer steps r (for $r=0$ to $\frac{1}{2}$) is $l=(1+2r)b$ and the incommensurability $\Delta=r/(1+2r)$. This model is perfectly ordered, whereas our ground-state model has different terrace lengths associated with different step heights. This serves to introduce a distinction between singles and triples in the diffraction process. However, if we calculate the diffraction pattern for a model with two terrace lengths, we again obtain excellent agreement with experimentally observed diffraction pattern as long as the ratio of terrace is not far from 1. If we allow the ratio of two terrace lengths to increase to 2, then the disorder in the structure becomes serious enough that the diffraction beams broaden and decrease in intensity, as predicted for a highly disordered structure [14]. The difference in the calculated variations of the beam position with step density for the two model cases is illustrated by solid and dashed curves in Fig. 4. The agreement of the model calculation with the measurements is shown in Table II, and in Fig. 4. Thus the observed LEED pattern reflects the average terrace length in a random mixture of singles and triples, and in this case diffraction is not sufficient to characterize the structure uniquely. Direct observation of the step sequence and terrace-length distribution is necessary.

In summary, we have observed step-height mixtures varying in triple density from 10% to 75% over a 5° range of surface misorientation angle, with no evidence of orientational phase separation. The wide range of misorientation angles for which we observe step-height mixtures contrasts with the much discussed case of step-height mixtures on vicinal Si(100) where only, at most, a narrow range is observed [2,3,7,25]. The difference can be understood [4] from the different nature of step-step interactions between single-layer steps on Si(001) [2] due to the anisotropy of the (2×1) reconstruction. In our case, the step-step interactions are governed by a simple prediction of elasticity theory that the strength of the repulsive interaction between steps should scale with the step heights. This is confirmed by our STM observation of a trimodal terrace-length distribution, with peak positions in excellent quantitative agreement with the values predicted [Eq. (2)] for elastically interacting steps.

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[1] For a review, see E. D. Williams and N. C. Bartelt, Science **251**, 393 (1991).

[2] O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **64**, 2404 (1990).

[3] X. Tong and P. A. Bennett, Phys. Rev. Lett. **67**, 101 (1991).

[4] E. Pehlke and J. Tersoff, Phys. Rev. Lett. **67**, 465 (1991).

[5] N. C. Bartelt, T. L. Einstein, and C. Rottman, Phys. Rev. Lett. **66**, 961 (1991).

[6] T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990).

[7] J. J. de Miguel, C. E. Aumann, R. Kariotis, and M. G. Lagally, Phys. Rev. Lett. **67**, 2830 (1991).

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

[9] J. M. Blakely and R. L. Schwoebel, Surf. Sci. **26**, 321 (1971).

[10] M. B. Webb, F. K. Men, R. Kariotis, and M. G. Lagally, Surf. Sci. **242**, 23 (1991).

[11] X.-S. Wang, J. L. Goldberg, N. C. Bartelt, T. L. Einstein, and E. D. Williams, Phys. Rev. Lett. **65**, 2430 (1990).

[12] C. Alfonso, J. M. Bermond, J. C. Heyraud, and J. J. Métois, Surf. Sci. **262**, 371 (1992).

[13] P. Bak, Rep. Prog. Phys. **45**, 587 (1982).

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

[15] R. Q. Hwang, E. D. Williams, and R. L. Park, Rev. Sci. Instrum. **60**, 2945 (1989).

[16] R. J. Phaneuf and E. D. Williams, Phys. Rev. B **41**, 2991 (1990).

[17] B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, J. Vac. Sci. Technol. A **7**, 2901 (1989).

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

[19] J. Wei and E. D. Williams (to be published).

[20] V. I. Marchenko and A. Ya. Parshin, Zh. Eksp. Teor. Fiz. **79**, 257 (1980) [Sov. Phys. JETP **52**, 129 (1980)].

[21] P. Nozieres, "Lectures Given at the Beg-Rohu Summer School," 1989 (unpublished).

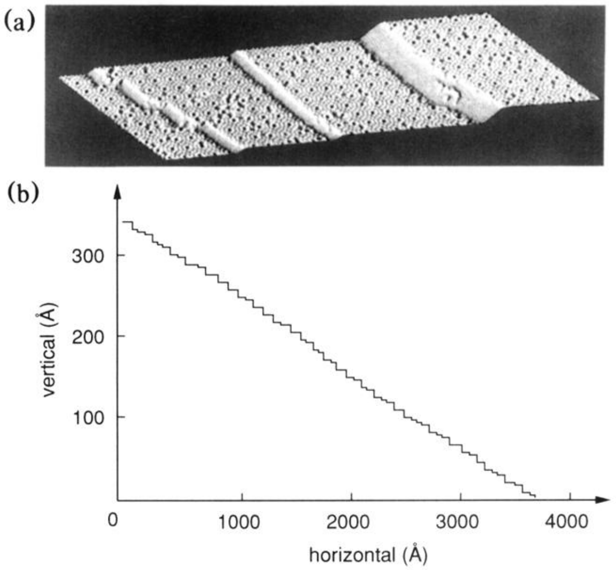
[22] We are using the term "torque" to describe both the in- and out-of-surface plane components of the elastic dipole forces at the step edge [21].

[23] N. C. Bartelt (unpublished).

[24] D. J. Srolovitz and J. P. Hirth, Surf. Sci. **255**, 111 (1991).

[25] C. C. Umbach, M. E. Keeffe, and J. M. Blakely, J. Vac. Sci. Technol. A **9**, 1014 (1991).

[26] J. L. Goldberg, X.-S. Wang, J. Wei, N. C. Bartelt, and E. D. Williams, J. Vac. Sci. Technol. A **9**, 1868 (1991).



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