Chapter 3. Step Structures and Epitaxy on Semiconductor Surfaces

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3.1 Introduction

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Surface morphology is key to a number of technologically important processes, including, for example, corrosion, catalysis and epitaxial growth. A striking change in the morphology of a crystal surface occurs at a *faceting transformation,* in which an initially uniform surface separates into regions with different surface orientations. An example of a surface that has undergone thermodynamic faceting is illustrated in figure 1, which shows an atomic force microscopy (AFM) image of a stepped Si(113) surface, misoriented from the [113] direction by 2.1° towards [001]. As may be seen, the surface morphology consists of grooves, each of which is in fact comprised of a (113) and a (114) facet. In general, the morphology for a given temperature and macroscopic misorientation may be specified by means of an *orientational phase diagram,* which is analogous to the phase diagram of a fluid, with the surface orientation (or step density) corresponding to the particle density.[1] In this context, faceting is a first-order phase transformation, and the image seen in figure 1 represents phase coexistence between (113) and (114) facets, which are distinct orientational phases.[2]

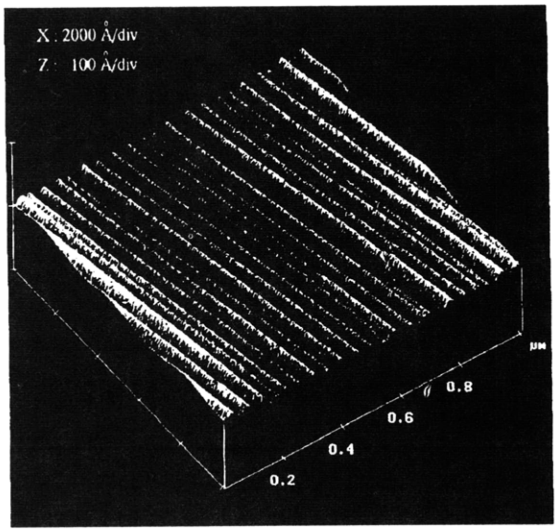

Figure 1. Grey-scale *ex situ* atomic force microscopy image of a stepped Si(113) surface misoriented by 2.1° toward [001] after annealing at 900 K. The sides of each groove are formed of a (113) facet and (114) facet. Note that the vertical scale is much exaggerated compared to the horizontal scales.

In addition to scientific motivations for studying faceting, an understanding of faceting may eventually allow for the introduction of simple processing strategies for tailoring surface morphology to suit technological needs. For example, recently it has been shown within the MIT JSEP program that the use of silicon substrates with a three-dimensionally grooved morphology decreases the dislocation

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[1] R.J. Phaneuf and E.D. Williams, *Phys. Rev. Lett.* 58: 2563 (1987); E.D. Williams and N.C. Bartelt, *Sci.* 251: 393 (1991); J.C. Heyraud, J.J. Metois, and J.M. Bermond, *J. Cryst. Growth* 98: 355 (1989); P. Nozieres, *J. Phys. France* 50: 2541 (1989); G.M. Watson, D. Gibbs, D.M. Zehner, M. Yoon, and S.G.J. Mochrie, *Phys. Rev. Lett.* 71: 3166 (1993); M. Yoon, S.G.J. Mochrie, D.M. Zehner, K.G. Huang, and D. Gibbs, *Phys. Rev. B* 49: 16702 (1994); J.S. Ozcomert, W.W. Pai, N. Bartelt, and J.E. Reutt-Robey, *Phys. Rev. Lett.* 72: 258 (1994).

[2] C. Rottman and M. Wortis, *Phys. Rev. B* 29: 328 (1984); C. Jayaprakesh and W.F. Saam, *Phys. Rev. B* 30: 3916 (1984); C. Jayaprakesh, C. Rottman, and W.F. Saam, *Phys. Rev. B* 30: 6549 (1984); C. Rottman, M. Wortis, J.C. Heyraud, and J.J. Metois, *Phys. Rev. Lett.* 52: 1009 (1984).

density of epitaxially grown GaAs films.[3] One may also suppose that surfaces, like that shown in figure 1, might be suitable templates for the growth of quantum wires or nano-crystal arrays.

Over the last one-year period, the goal of our JSEP research has been to elucidate and understand the orientational phase diagram of certain surfaces of silicon—namely stepped Si(113) surfaces—and also to understand the kinetics of the faceting process. To this end, we have carried out a comprehensive x-ray scattering study of stepped Si(113) surfaces as a function of the sample temperature and misorientation angle, which is equivalent to the step density. We have also studied the evolution of surface morphology following a temperature jump (quench) from a temperature where the surface is uniformly stepped to a temperature where it is faceted. Our experiments were performed at the National Synchrotron Light Source (NSLS) with MIT-IBM beamlines at X20 and NSLS beamlines at X25. For these experiments, we used our ultra-high-vacuum apparatus for surface x-ray scattering. Important new insight into the mechanism of faceting has emerged from these studies.[4]

3.2 Phase Behavior of Stepped Si(113) Surfaces

For fluids, at the appropriate conditions of temperature and density, attractive interactions between the constituent particles of the fluid lead to the condensation of a liquid phase in coexistence with a vapor. It is natural then to expect that for attractive interactions between steps, "step condensation"—that is faceting—might occur. Prior to our experiments, such a possibility had been predicted theoretically, but not observed. In the case of a fluid, special interest attaches to the critical point, in part, because of the dramatic variation of fluid properties that occurs nearby, and, in part, because the critical exponents that characterize this behavior are universal. Just as a near-critical fluid exhibits critical opalescence, so might a surface with mutually attracting steps show critical step fluctuations that are manifest as a divergent surface roughness. Such a step critical behavior seems remarkable, but nevertheless was observed and characterized in our recent experiments.

Specifically, we studied stepped Si surfaces miscut away from the [113] direction towards [001].[5] The phase diagram deduced from our measurements is shown in figure 2. The solid lines indicate phase boundaries; while the solid circles and squares represent mesoscopic surface orientations measured for samples with macroscopic misorientations of 2.1° and 3.7°, respectively. The (113) orientation, located at zero misorientation angle, is a stable phase for all temperatures studied.[6]

Above 1223 K and at non-zero misorientation angles, there occurs a one-phase region of the phase diagram, in which the surface is uniformly stepped. We infer that the transformation versus orientation between the stepped phase and the (113) facet occurs smoothly and continuously above 1223 K.[7] In this region, we find strongly temperature-dependent diffuse scattering, which may indeed be identified as critical scattering, and is the result of an increase in step fluctuations with decreasing temperature. Figure 3 highlights the step critical scattering for several temperatures above 1223 K on a log-log scale versus κ. (κ is the component of the scattering wave-vector parallel to the surface.) The lineshape for $\kappa < 0.005$ is determined by the resolution. However, the scattering that appears for $\kappa > 0.005$ is the step critical scattering of interest. The inset illustrates that the surface stiffness ($\tilde{\gamma}$), which is inversely proportional[8] to the intensity of this critical scattering varies as a power-law versus reduced temperature with respect to a spinodal line: $\tilde{\gamma} = \tilde{\gamma}_0 t_s^{\lambda}$, with $\lambda = 0.76 \pm 0.2$, $\tilde{\gamma} = (56 \pm 20) k_B T c^{-2}$, and $t_s = (T - T_s(\theta))/T_s(\theta)$.

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[3] L.A. Kolodziejski, H.I. Smith, and C.V. Thompson, *RLE Progress Report* 136: 88 (1993).

[4] S. Song and S.G.J. Mochrie, *Phys. Rev. Lett.* 73: 995 (1994); S. Song, S.G.J. Mochrie, and G.B. Stephenson, in preparation (1995).

[5] S. Song and S.G.J. Mochrie, *Phys. Rev. Lett.* 73: 995 (1994); S. Song and S.G.J. Mochrie, *Phys. Rev. B* (forthcoming).

[6] D.L. Abernathy, *An X-ray Scattering Study of the Si(113) Surface: Structure and Phase Behavior,* Ph.D. diss., Dept. of Phys., MIT, 1993.

[7] C. Rottman and M. Wortis, *Phys. Rev. B* 29: 328 (1984); C. Jayaprakesh and W.F. Saam, *Phys. Rev. B* 30: 3916 (1984); C. Jayaprakesh, C. Rottman, and W.F. Saam, *Phys. Rev. B* 30: 6549 (1984); C. Rottman, M. Wortis, J.C. Heyraud, and J.J. Metois, *Phys. Rev. Lett.* 52: 1009 (1984).

[8] A. Braslau, M. Deutsch, P.S. Pershan, A.H. Weiss, J. Als-Nielsen, and J. Bohr, *Phys. Rev. Lett.* 54: 114 (1985); M. Sanyal, S.K. Sinha, K.G. Huang, and B.M. Ocko, *Phys. Rev. Lett.* 66: 628 (1991).

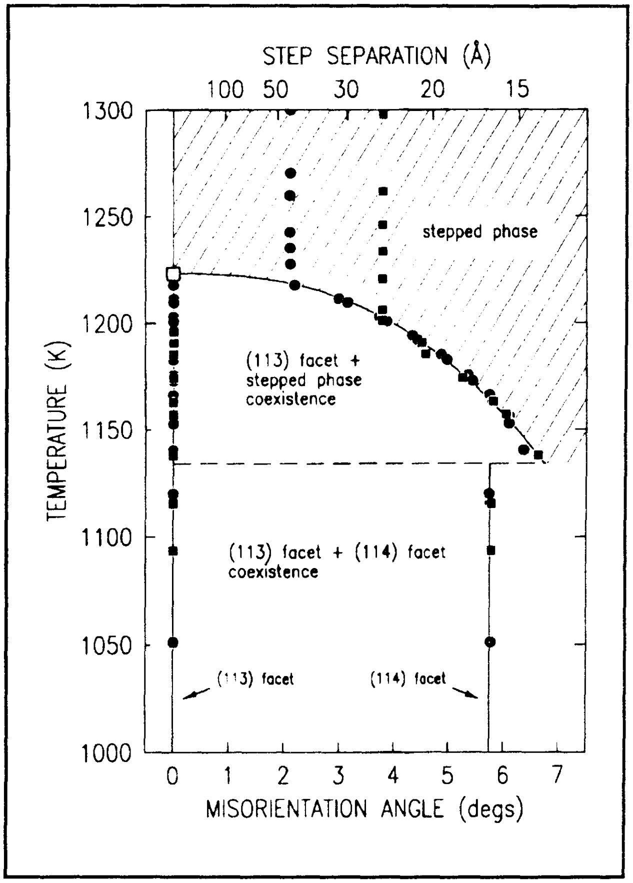

Figure 2. Orientational phase diagram of stepped Si(113) surfaces misoriented towards [001] versus temperature and misorientation angle. The one-phase region is hatched; two-phase regions are unhatched solid lines are phase boundaries. The dashed line corresponds to the triple point. Solid circles and solid squares show the mesoscopic misorientations measured for samples with macroscopic misorientations of 2.1° and 3.7°, respectively.

The step critical scattering anticipates a faceting transformation at which the surface transforms from a homogeneous phase of uniform orientation into coexisting phases with different orientations. Between 1223 and 1130 K, there is a two-phase region, so that the transformation versus orientation between the stepped phase and the (113) facet is first-order. The range of angles forbidden to the stepped phase (θ) may also be described as a power-law versus reduced temperature (shown as a solid line in figure 2): $\theta = \theta_0 t^{\beta}$, with $\beta = 0.42 \pm 0.10$, $\theta_0 = 21 \pm 6°$, and $t = (T_t - T)/T_t$, with $T_t = 1223$ K. The point in a phase diagram that separates a line of continuous transformations from a line of first-order transformation is a *tricritical point.* Thus, the point at $T_t = 1223$ K and zero misorientation angle is a tricritical point (open square in figure 2). To our knowledge, the present example is the first experimental observation of a tricritical point in an orientational phase diagram.

Finally, below a triple point temperature of $T_3 = 1130 \pm 10$K (dashed line in figure 2), coexistence between the (113) facet and the (114) facet, which lies 5.7° from the [113] direction, replaces coexistence between the (113) facet and the stepped phase.

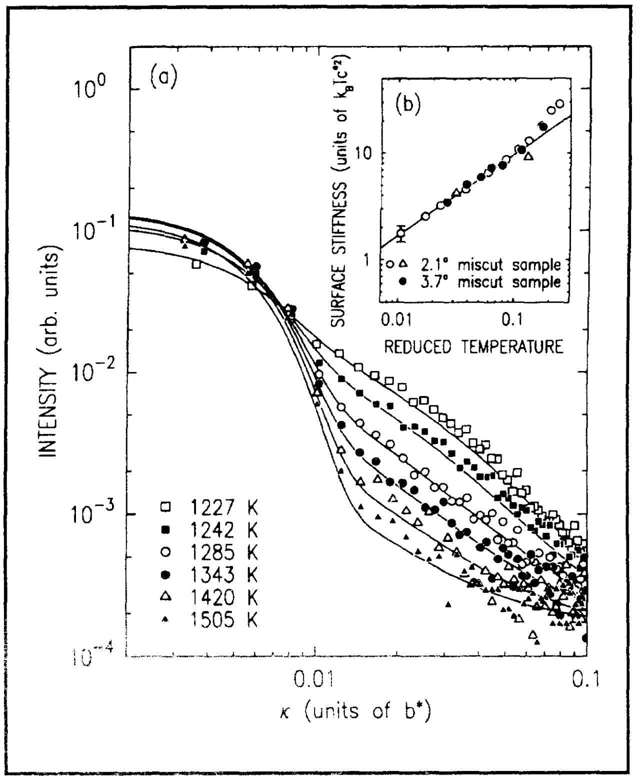

Figure 3. Log-log plot of the scattered intensity vs. κ for the 2.1° miscut sample at L = 2 for several temperatures in the one-phase region. Solid lines are a model lineshape based on the capillary mode model for surface roughness. The inset shows that the surface stiffness, deduced from fits to the model lineshape, varies as a power law versus reduced temperature.

3.3 Faceting Kinetics of Stepped Si(113) Surfaces: Self-Assembled Nano-Scale Gratings

Most recently, we have studied the behavior following a quench from the uniformly stepped phase (hatched in figure 2) into the coexistence region (unhatched in figure 2), using time-resolved x-ray scattering techniques.[9] The kinetics of phase separation is a topic of considerable and growing interest.[10] After a quench, domains of the low-temperature phase first form and then "coarsen," becoming larger and larger with time. It is generally expected that the coarsening process exhibits *dynamic scaling,* so that the system at a time t is characterized by a single time-dependent length which grows as a power law versus time, i.e., $L \sim t^{\phi}$. Analogous to critical behavior, the value of ϕ and of other exponents is expected to be characteristic of the kinetic universality class in question, which itself depends on the dimensionality of space, the symmetry of the order parameter, and the applicable conservation laws. Most systems studied to date correspond to a scalar order parameter for which $\phi = 1/2$ or $1/3$ for a conserved or a non-conserved order parameter, respectively.

Figure 4 shows the intensity versus the wavevector transfer parallel to the surface, obtained at several times up to 1200 seconds, using a linear detector following a quench of a 2.1° misoriented sample from a temperature of 1240 K in the one-phase region to a temperature of 1173 K in the two-phase region.[11] The intense peak at zero wavevector (figure 4a) corresponds to specular reflection. Evidently, following the quench the specular peak decreases in intensity as a result of the increasing surface roughness. By 1200 seconds after the quench, the specular peak has decreased by a factor of approximately two.

The peaks symmetrically located about the specular peak (figure 4b) constitute the first-order diffraction scattering from the "grating" of figure 1. It is evident that with increasing time, these peaks grow in intensity, shift to smaller wavevector, and become narrower. This behavior is reminiscent of that observed at small angles when a binary alloy or binary fluid is quenched into the coexistence region. In that case, the small angle scattering originates in the correlated domain structure of the phase separation mixture. Similarly, the scattering of figure 4 is a result of finite-sized (113) facets in coexistence with densely stepped regions. The peak shift to smaller wavevectors corresponds to an increase in the separation and size of these domains with increasing time. Further quenching to room temperature allows us to freeze in any groove rise between 400 and 1500 Å. Detailed fitting reveals that the peak width decreases approximately proportionately to the peak position. This is particularly interesting in view of the facts that the system in question is two-dimensional and corresponds to a kinetic universality class that has not previously been investigated experimentally. Of additional special interest is that the exponent φ for the facet coarsening process takes the value $\varphi = 0.1625 \pm 0.015$, which is very different from 1/3 or 1/2.

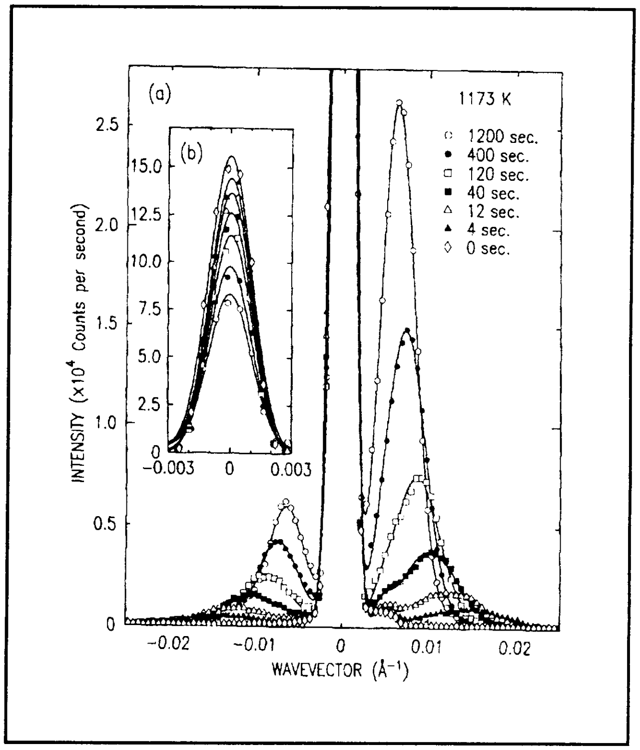

Figure 4. Scattering versus temperature for stepped Si(113) surface at several different times up to 120 seconds following a quench from 1240 to 1173 K.

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[9] G.B. Stephenson, *Nucl. Instr. Meth. Phys. Res.* A266: 447 (1988).

[10] J.D. Gunton, M.S. Miguel, and P.S. Sahni in *Phase Transitions and Critical Phenomena* Vol. 8, eds. C. Domp and J. L. Lebowitz (Academic Press, New York, 1983); S.N. Majumdar, D.A. Huse, and B.D. Lubachevsky, *Phys. Rev. Lett.* 73: 182 (1994).

[11] S. Song, S.G.J. Mochrie, and G.B. Stephenson, in preparation (1995).

3.4 Publications

Abernathy, D.L., S. Song, K.I. Blum, R.J. Birgeneau, and S.G.J. Mochrie. "Chiral Melting of the Si(113) (3 X 1) Reconstruction." *Phys. Rev. B* 49: 2691 (1994).

Song, S., and S.G.J. Mochrie. "Attractive Interactions Between Steps, Tricriticality and Faceting in the Orientational Phase Diagram of Silicon Surfaces Between (113) and (114)." *Phys. Rev. B.* Forthcoming.

Song, S., and S.G.J. Mochrie. "Tricriticality in the Orientational Phase Diagram of Stepped Si(113) Surfaces." *Phys. Rev. Lett.* 73: 995 (1994).