

Chapter 3. Step Structures and Epitaxy on Semiconductor Surfaces

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3.1 Introduction

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There is at present considerable effort directed towards the fabrication of nanoscale semiconductor objects. This is, in part, to allow for the investigation of the behavior of electrons within structures of sufficiently small dimensions to produce quantum confinement. Such so-called *quantum dots* and *quantum wires* typically have dimensions of a few hundred Angstroms. In addition, quantum dots and wires have been proposed as a route to many new device applications.

Recently, it has emerged that nanoscale structures on certain semiconductor surfaces may spontaneously self-assemble into more-or-less ordered patterns. Over the last year, we have been pursuing investigations of two examples of this phenomenon. Our goal is to achieve a microscopic and predictive understanding of the factors that determine the nanostructure and how it may be controlled and exploited in the creation of new nanoscale surface structures, for example, by decoration schemes to create chemically heterogeneous surfaces. Specifically, we have completed a comprehensive study of the self-assembly of nanoscale grooves on stepped silicon surfaces. In addition, we have continued studies of Ge quantum dots on Si.

Self-assembly of nanoscale grooves on stepped Si(113) faceting is a remarkable phenomenon in which a crystal surface increases its area in order to decrease its free energy. This is accomplished via the rearrangement of surface steps into regions

of low and high step density. Stepped Si(113) surfaces realize a new paradigm for the thermodynamics and kinetics of faceting and the way elasticity determines surface morphology.

The phase diagram of silicon surfaces miscut from the $[113]$ direction towards $[001]$ is shown in figure 1 versus temperature and miscut angle. The (113) orientation—at zero misorientation angle—is a stable phase for all temperatures studied. 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. In this region, we find strongly temperature-dependent, near-specular diffuse scattering, which is critical scattering, and is the result of an increase in step fluctuations with decreasing temperature. 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. The point at $T_1 = 1223$ K and zero misorientation (open square in figure 1) angle is actually a special type of critical point called a tricritical point. Below a triple point temperature of $T_3 = 1130 \pm 10$ K (dashed line in figure 1), coexistence between the (113) facet and the (114) facet, which lies 5.7 degrees from the $[113]$ direction, replaces coexistence between the $[113]$ facet and the stepped phase. This work inspired two independent theoretical investigations aimed at understanding our observations which recently appeared in *Physical Review Letters*¹ and which relate the step tricritical behavior to a two-dimensional "wetting" transition, occurring in the presence of long-ranged repulsions and short-ranged attractions between steps.

In fact, upon faceting, the stepped Si(113) surfaces described above spontaneously form a striking

¹ M. Lassig, *Phys. Rev. Lett.* 77: 526 (1996); S. Bhattacharjee, *Phys. Rev. Lett.* 76: 4568 (1996)

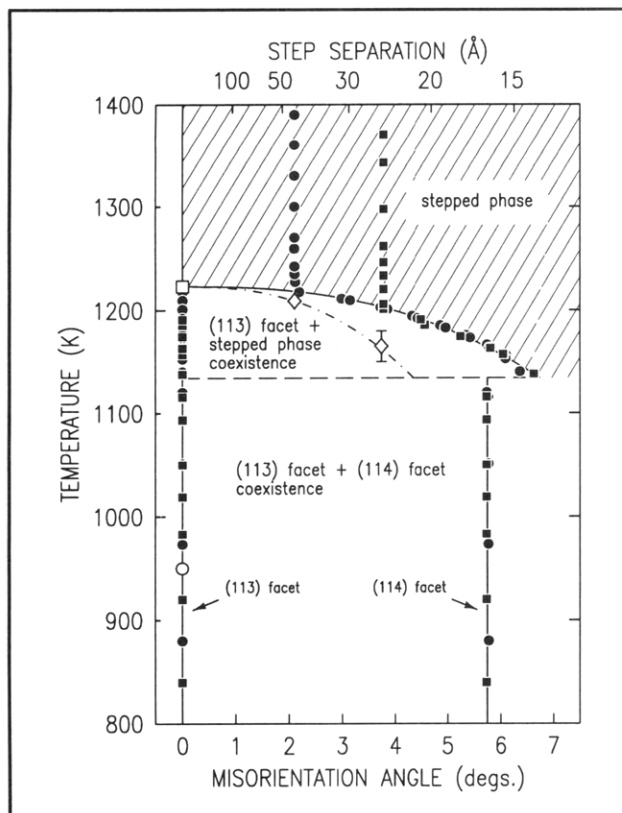


Figure 1. Orientational phase diagram of stepped Si(113) surfaces misoriented towards [001]. Solid lines indicate phase boundaries; solid circles and squares represent mesoscopic surface orientations measured for samples with macroscopic misorientations of 2.1 degrees and 3.7 degrees, respectively.

mesoscopically grooved morphology.² Figure 2 shows an *ex-situ* atomic force microscope (AFM) image of one such surface. Here, one side of each groove is a step-free (113) facet and the other side is a step bunch. Individual grooves are a few hundred Angstroms across and exceed one micron in length. Evidently, the grooves self-assemble to form the nearly periodic nanoscale grating that may be seen in the figure. Practical interest derives from the fact that it is very difficult to make such

small structures using lithography. Indeed, considerable interest is emerging in employing our grooved silicon surfaces as a template for nanolithography.

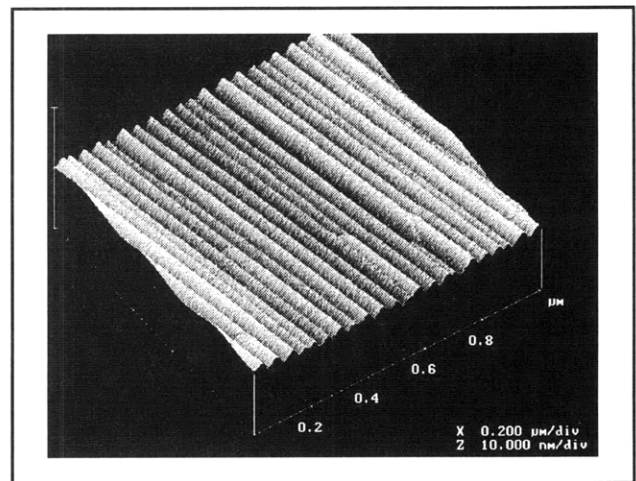


Figure 2. AFM image of a 10000 X 10000 Å² area of a self-assembled grating on a stepped Si(113) surface. One side of each groove is step-free, the other side is densely-stepped.

Associated with the grating of figure 2 are first-order diffraction peaks. The peak locations are determined by the grating periodicity and the peak widths by the degree of ordering. As illustrated in figure 3, with increasing time, these peaks grow in intensity, shift to smaller wave vectors, corresponding to an increase in the groove period, and become narrower, corresponding to an increasingly ordered structure. The peak positions and widths (HWHM) of the first-order diffraction peaks are shown on a log-log scale versus time for three representative final temperatures in figure 4. The variation of the peak position versus time is consistent with a 1/6 power-law behavior for times between a few and several hundred seconds. These results have led to a theory of the growth of grooves, which reproduces the 1/6 power-law and identifies the rate-limiting step as the close approach of neighboring step bunches.

² S. Song and S.G.J. Mochrie, *Phys. Rev. B* 51: 10068 (1995).

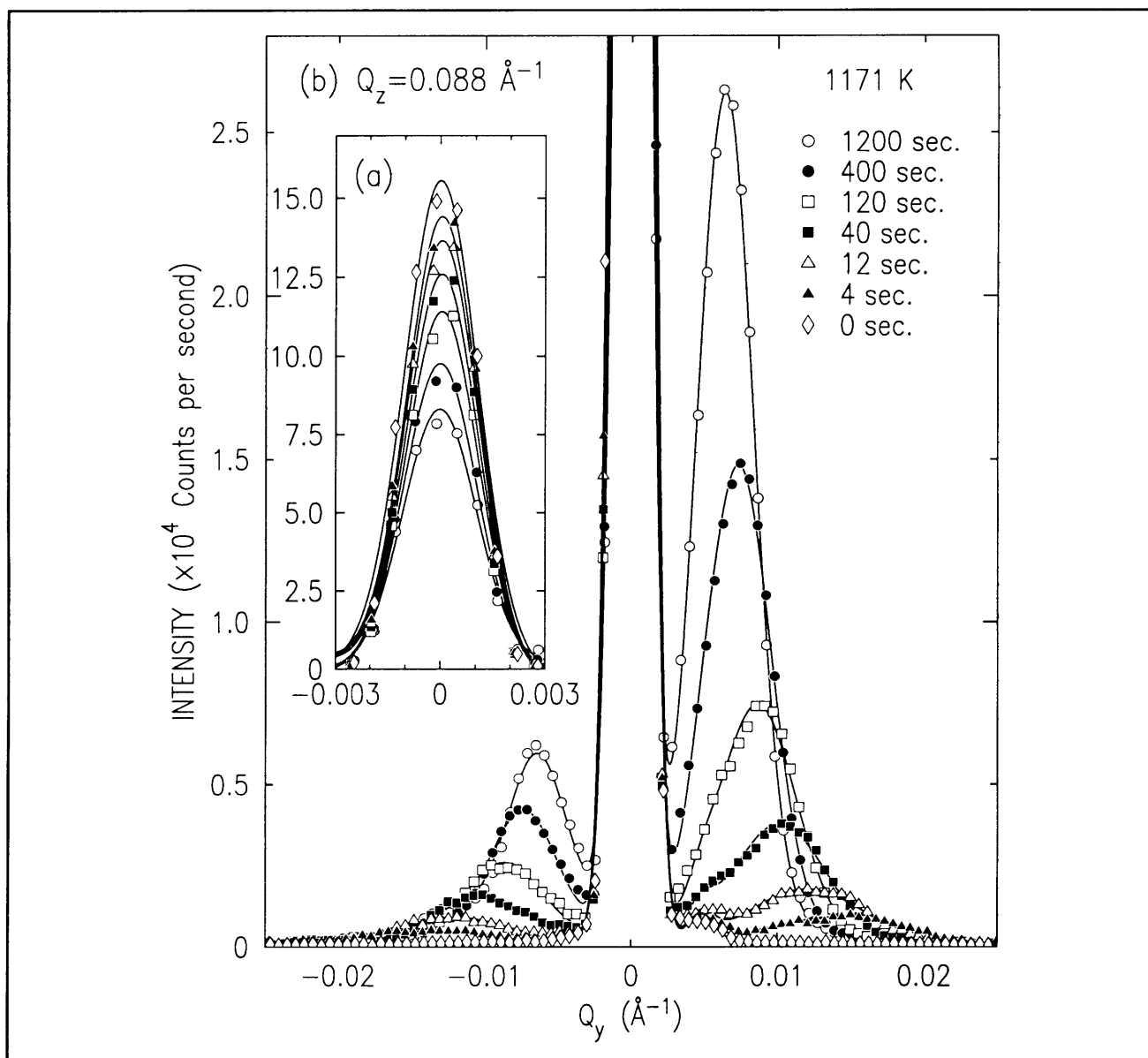


Figure 3. Time evolution of the first-order diffraction peaks of the structure shown in figure 2, following a temperature quench from 1248 to 1171 K.

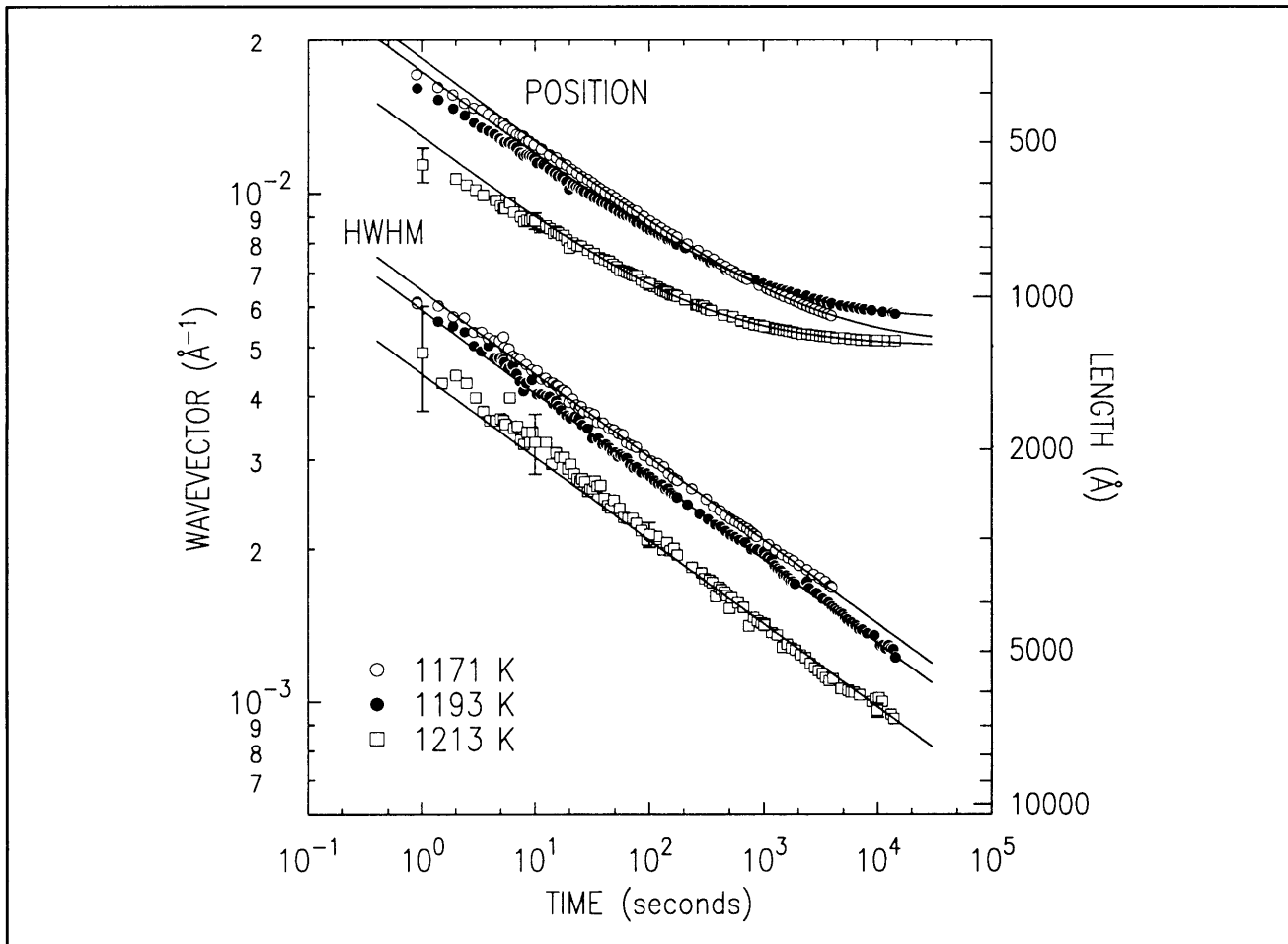


Figure 4. Log-log plot of the position and HWHM of the first-order diffraction peaks for three representative quench temperatures.

A key prediction of the theory is that the characteristic length scale along the grooves—i.e., the length of the grooves—varies as a 1/2-power law versus time. We have recently initiated experiments to test this important prediction. A preliminary analysis indicates agreement with theory.

At longer times the groove size approaches a constant value while the groove ordering continues to improve, indicating that the surface morphology is evolving towards a periodic, ordered equilibrium state. The variation of the limiting facet size versus the stepped phase misorientation angle may be understood qualitatively on the basis of Marchenko et al.³, where it is proposed that the lowest energy configuration of a faceted surface corresponds to a periodically grooved morphology.

The special stability of the grooved structure originates in a reduction of surface-stress-induced elastic energy in the bulk that occurs for mesoscopic facets as compared to macroscopic facets. The period is determined by balancing the reduction in elastic energy against the cost in energy of maintaining edges between the coexisting phases. The theory predicts that the groove period is minimized when the angles between each side of the groove and the macroscopic surface are equal, as found experimentally for the two differently misoriented samples. Thus, we have achieved an in-depth understanding of the mechanism responsible for nanoscale grooves on stepped Si(113) surfaces.

In conclusion, we have achieved a very complete understanding of why and how nanoscale grooves form on stepped Si(113) surfaces. Since faceting is

³ V.I. Marchenko, *Zh. Eksp. Teor. Fiz.* 81: 1141 (1981); *Sov. Phys. JETP* 54: 605 (1981); O.L. Alerhand, D. Vanderbilt, R.D. Meade, and J.D. Joannopoulos, *Phys. Rev. Lett.* 61: 1973 (1988).

a widespread phenomenon, we may be confident that the understanding gained here will have widespread application to other surfaces and materials. For example, we are presently analyzing the results of x-ray scattering experiments on Si(112), which spontaneously undergoes faceting to produce a grooved superstructure.

3.1.1 Self-assembly of Ge Quantum Dots on Si(001)

The manufacture of quantum dots and wires is exceedingly difficult. For example, it is difficult to achieve the requisite sizes with lithography. Schemes which directly build quantum-sized objects during growth are possible alternatives. Such schemes include, for example, cluster formation in the gas phase and subsequent cluster deposition, and growth on patterned substrates such as stepped surfaces.

An especially promising and interesting approach is the self-assembly of a nanostructure during strained heteroepitaxial growth on a flat substrate. Strained heteroepitaxial growth, involving a large lattice mismatch, generally proceeds via the formation of islands after the initial growth of a few flat layers. Recently, Krishnamurthy et al., Leonard et al., and Moison et al.⁴ have found that it is possible to prepare near-uniformly sized and near-uniformly spaced islands of dislocation-free Ge on Si(001), InGaAs on GaAs(001), and InAs on GaAs(001), respectively. It is this apparent self-organization of defect-free quantum dots that is so remarkable from both a technological and a scientific viewpoint. However, a fundamental understanding of quantum dot formation—whether it is kinetic or thermodynamic in origin—is presently lacking.

In the earlier studies, it was not possible to examine *in-situ* island formation during the deposition and annealing processes. By contrast, we have initiated an investigation of the *in-situ* self-assembly of quantum dots of germanium on silicon as it occurs. We use both synchrotron x-ray scattering techniques to monitor how the surface morphology develops in real-time and the atomic force microscope to take definitive "snap shots" of the surface morphology by means of rapid temperature quenches. In this way, we hope to achieve a microscopic and predictive understanding of the factors that determine the final morphology. As a

result, we expect to learn how to control the nanostructure.

We have chosen to study, initially, the Ge-on-Si system, in part because of the earlier work of Krishnamurthy et. al., and in part because of the potential utility of Ge-Si heterostructures in device applications. Figure 5 illustrates an AFM image of a surface upon which is deposited the equivalent of approximately 8 monolayers of Ge at a substrate temperature of 480 K.

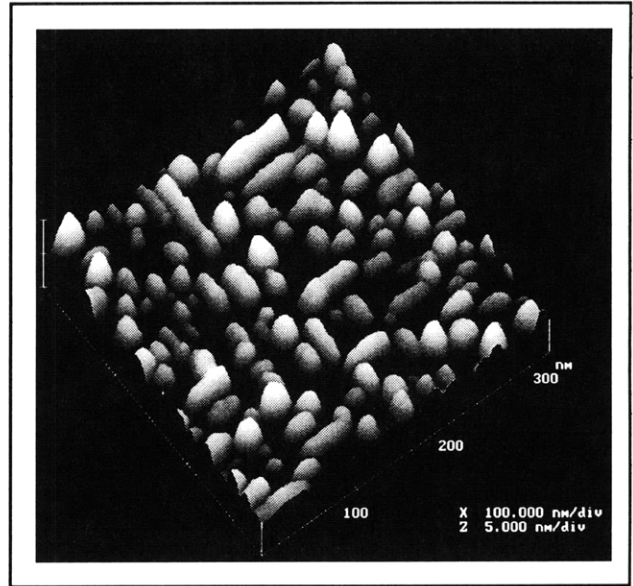


Figure 5. AFM image of Ge quantum dots on Si(001)

Three monolayers grow in a layerwise fashion, but subsequent deposition occurs in the form of three dimensional islands—quantum dots—which may be clearly seen in the image more-or-less uniformly spaced across the surface. This figure demonstrates that we can prepare quantum dots for study. As may be seen, some of the dots are elongated along two orthogonal directions, which are high symmetry directions of the substrate. This interesting aspect is not understood.

The development of the morphology seen in figure 5 may be monitored *in situ* and in real time using synchrotron x-ray scattering. This is demonstrated in figure 6, which shows x-ray scattering results we obtained recently during Ge deposition on a Si(001) substrate, over the course of 2000 seconds at a substrate temperature of 480 K, for coverages that are equivalent to between approximately 1 and 8 monolayers. The two peaks symmetrically located

⁴ M. Krishnamurthy, J. Drucker, and J.A. Venables, *J. Appl. Phys.* 69: 6461 (1991); D. Leonard et al., *J. Vac. Sci. Technol.* B 12: 1063 (1994); J.M. Moison et al., *Appl. Phys. Lett.* 64: 196 (1994).

around the central specular peak derive from Ge quantum dots as they appear on the surface. Specifically, the separation from the specular peak determines the separation of quantum dots on the surface.

We are currently investigating the evolution of the surface morphology versus time at different deposition temperatures and for different Ge coverages and temperatures subsequent to deposition. Of special interest are the degree to which the dots are the same size and the extent of their ordering.

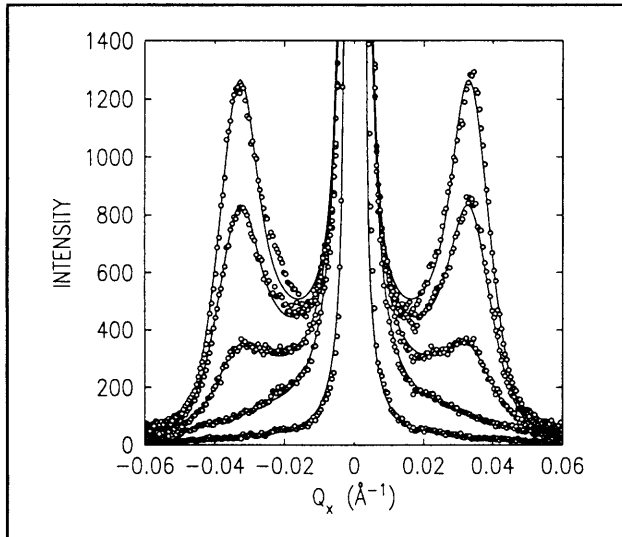


Figure 6. Diffraction peaks due to Ge quantum dots during deposition at 480 K.

3.2 Publications

Bhattacharjee, S.M. "Theory of Tricriticality for Miscut Surfaces." *Phys. Rev. Lett.* 76(24): 4568 (1996).

Lässig, M. "Vicinal Surfaces and the Calogero-Sutherland Model." *Phys. Rev. Lett.* 77(3): 526 (1996).

Mochrie, S.G.J., S. Song, M. Yoon, D.L. Abernathy, and G.B. Stephenson. "Faceting of Stepped Silicon (113) Surfaces: Self Assembly of Nano-scale Gratings." *Physica B* 221: 105 (1996).

Song, S., M. Yoon, S.G.J. Mochrie, and G.B. Stephenson. "Faceting Kinetics of Stepped Si(113) Surfaces: Dynamic Scaling and Nano-scale Grooves." *Surf. Sci.* Forthcoming.

3.2.1 Thesis

Song, S. *Faceting and Tricriticality in the Orientational Phase Diagram of Stepped Si(113) Surfaces: Synchrotron X-ray Scattering Studies.* Dept. of Phys., MIT, 1996

3.2.2 Invited Talks

Mochrie, S.G.J. "Faceting of Stepped Si(113): Step Unbinding, Dynamic Scaling, and Self-Assembly of Nano-scale Grooves." Conference on the Dynamics of Crystal Surfaces and Interfaces, Traverse City, Michigan, August 1996.

Mochrie, S.G.J. "Faceting of Stepped Si(113): Step Unbinding, Dynamic Scaling, and Self-Assembly of Nano-scale Grooves." Fall Meeting of the Materials Research Society, Boston, Massachusetts, December 1996.