

Chapter 2. Synchrotron X-Ray Studies of Surface Disordering

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2.1 Introduction

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In this research program we use modern x-ray scattering techniques to study structures and phase transitions in thin films and on surfaces. We have two principal experimental facilities, one at MIT and the other at the National Synchrotron Light Source at Brookhaven National Laboratory. At MIT, we have four high-resolution computer-controlled x-ray spectrometers using high-intensity, rotating anode x-ray generators. The angular resolution can be made as fine as 1.8 seconds of arc, which enables us to probe the development of order from distances of the order of the x-ray wavelength $\sim 1\text{\AA}$ up to $30,000\text{\AA}$. The sample temperature can be varied between 2 K and 500 K with a relative accuracy of 2×10^{-3} K. At the National Synchrotron Light Source, in collaboration with IBM, we have three fully instrumented beam lines. Two of these beam lines allow us to make studies with photons varying in energy between 3 and 12 keV; the third has a fixed energy of 17 keV. These facilities make possible high-resolution scattering experiments with a flux of more than three orders of magnitude larger than that of a rotating anode x-ray generator, opening up a new generation of experiments.

Several years ago, as part of this JSEP program, we built an x-ray-compatible, high vacuum single crystal apparatus. This enabled us to use synchrotron radiation to study the structures and transitions occurring at a single surface, and such experiments are now becoming routine. As a result of our recent research, we determined that a new chamber allowing access to a wider range of reciprocal space was required. In collaboration with Professor Simon G.J. Mochrie, we have

designed, built and are now commissioning this second-generation x-ray surface facility.

Our basic scientific objective is to understand the morphologies and microscopic structures of simple semiconductor and metal surfaces at high temperatures. Possible phase changes include surface roughening, surface reconstruction, melting, amorphization and dilution. These phenomena are particularly interesting on stepped surfaces, where there may be an interplay between step structures, faceting, reconstruction, and roughening.

2.2 Metal Surface Studies

In 1987 we reported a detailed study of a possible roughening transition of the Ag(110) surface. Specifically, we discussed the detailed line shape of the Ag(110) surface peak for temperatures between 100°C and 525°C . At $\sim 450^\circ\text{C}$ we observed a crossover to a pure power law lineshape, indicative of a rough surface, for the near-surface diffraction. Above 450°C the profiles could be described by the power law singularity form $(Q - Q_{110})^{-2+\eta}$ with η changing rapidly with temperature. Accordingly, we identified 450°C as the roughening temperature.

Our more recent experiments and those by others on crystals with very small miscuts ($\sim 0.5^\circ$) suggest that the story may be more complicated. Specifically, the experiments suggest that below $\sim 450^\circ\text{C}$ to 500°C , the Ag(110) surface may be faceted. In order to explore this further, we have begun a systematic set of experiments on vicinal Ag(110) crystals with miscuts in the (110) direction of up to 4° . Our initial experiments on a crystal miscut by $\sim 2.3^\circ$ indeed show faceted behavior below $\sim 500^\circ\text{C}$. Further experiments should elucidate the full nature of the roughening-facetting transition on this prototypical noble metal surface.

2.3 Semiconductor Surface Studies

2.3.1 Stepped Si(111) Surfaces

The behavior of vicinal surfaces (surfaces cut a few degrees away from low index facets) involves essential aspects of surface structures including equilibrium crystal shapes, roughening, faceting, and surface reconstruction. The stability of vicinal surfaces is determined by the shape of the equilibrium crystal surface. By studying a series of vicinal surfaces with various surface normals, one can map out the equilibrium crystal shape. A vicinal surface, when it is stable, forms a structure consistent with low-index terraces separated by steps whose spacing is usually incommensurate with the bulk substrate lattice. As in the case of incommensurate domain wall problems, there can not be true long range order in the structure of the incommensurate steps. This is due to the overwhelming amplitude of the long wavelength thermal fluctuations in two-dimensional systems with continuous symmetry. As a result, an incommensurate stepped surface is rough in an exact sense. A vicinal surface becomes unstable when the free energy of a nearby low index facet is lowered drastically by some mechanisms such as reconstruction. One might expect that the lowering of free energy of a low-index facet would break a vicinal surface into a low-index facet and rough faces with a higher misorientation angle.

We have carried out a detailed synchrotron x-ray scattering study of a vicinal Si(111) surface misoriented by 3.5° toward the (112) direction. At temperatures higher than the "7 x 7-to-1 x 1" transition, we find that the surface is composed of steps with a mean separation of $\sim 60\text{\AA}$ which are correlated beyond 3000\AA . Below the transition, the surface is split into the large ($> 3000\text{\AA}$) perfectly flat (111) facets together with stepped regions whose misorientation angle increases as temperature is decreased. The transition is first order, indicating that it is induced by the 7 x 7 reconstruction of the (111) facets. In the faceted phase, the facet angle α follows the law $\tan \alpha \sim |T_c - T|^{(\lambda-1)/\lambda}$ with $\lambda = 2.3 \pm 0.3$. This disagrees somewhat with the theoretical prediction $\lambda = 3/2$ for models in which the interaction between steps is entropic in character.

At temperatures above 1110 K, we observed two step superlattice peaks bracketing the (10) position of the (111) surface. Figure 1 shows high resolution longitudinal and transverse scans through the first-order step peak at 1120 K. The simplest model leads us to believe that this peak results from the ordering of steps by the entropic

repulsion. To test this idea quantitatively, we fit the high temperature peak profile to a 2D power law singularity of the form

$$S(\vec{q}) = (q_H^2 + Bq_K^2)^{-(2+\eta_1)/2}$$

convolved with the instrumental resolution function. Figure 1 shows the optimal simultaneous fits to the longitudinal and transverse scans with $h = 0.6 \pm 0.1$ and $B = 15 \pm 7$. It is evident that the power law form fits the data very well. The large value of η_1 is fully consistent with scattering from a rough surface whose height variance diverges logarithmically with distance. We note that as in the stripe domain commensurate-incommensurate problem the Pokrovsky-Talapov model leads to the prediction $\eta_1 = 2/9$, independent of temperature. This is in clear disagreement with our results. More elaborate models of the interaction between the steps are needed to explain the large value of η_1 .

More recently, we have been studying the behavior of vicinal Si(111) at very high temperatures. Remarkably, we find that at ~ 1300 K there is a second phase transition in the step structure which mimics a surface melting transition. We are currently exploring this new-found phenomenon.

2.4 Publications

Blum, K.I., D.Y. Noh, A. Mak, K.W. Evans-Lutterodt, J.D. Broch, G.A. Held, and R.J. Birgeneau. "Structure and Phase Transitions of Ge(111) and Si(111) Surfaces at High Temperatures." In *Surface X-Ray and Neutron Scattering*. Vol. 61, pp. 27-31. Springer Proceedings in Physics. Ed. H. Zabel and I.K. Robinson. Berlin/Heidelberg: Springer-Verlag, 1992.

Keane, D.T., P.A. Bancel, G.L. Jordan-Sweet, G.A. Held, A. Mak, and R.J. Birgeneau. "Evidence for Two-Step Disordering of the Au(110) 1 x 2 Reconstructed Surface." *Surf. Sci.* 250: 8 (1991).

Mak, A., K. Evans-Lutterodt, K.I. Blum, D.Y. Noh, J.D. Brock, G.A. Held, and R.J. Birgeneau. "Synchrotron X-ray Diffraction Study of the Disordering of the Ge(111) Surface at High Temperatures." *Phys. Rev. Lett.* 66: 2002 (1991).

Noh, D.Y., K. Blum, M.J. Ramstad, and R.J. Birgeneau. "Long Range Separation of Steps on Vicinal Si(111)." *Phys. Rev. B* 44: 10969 (1991).

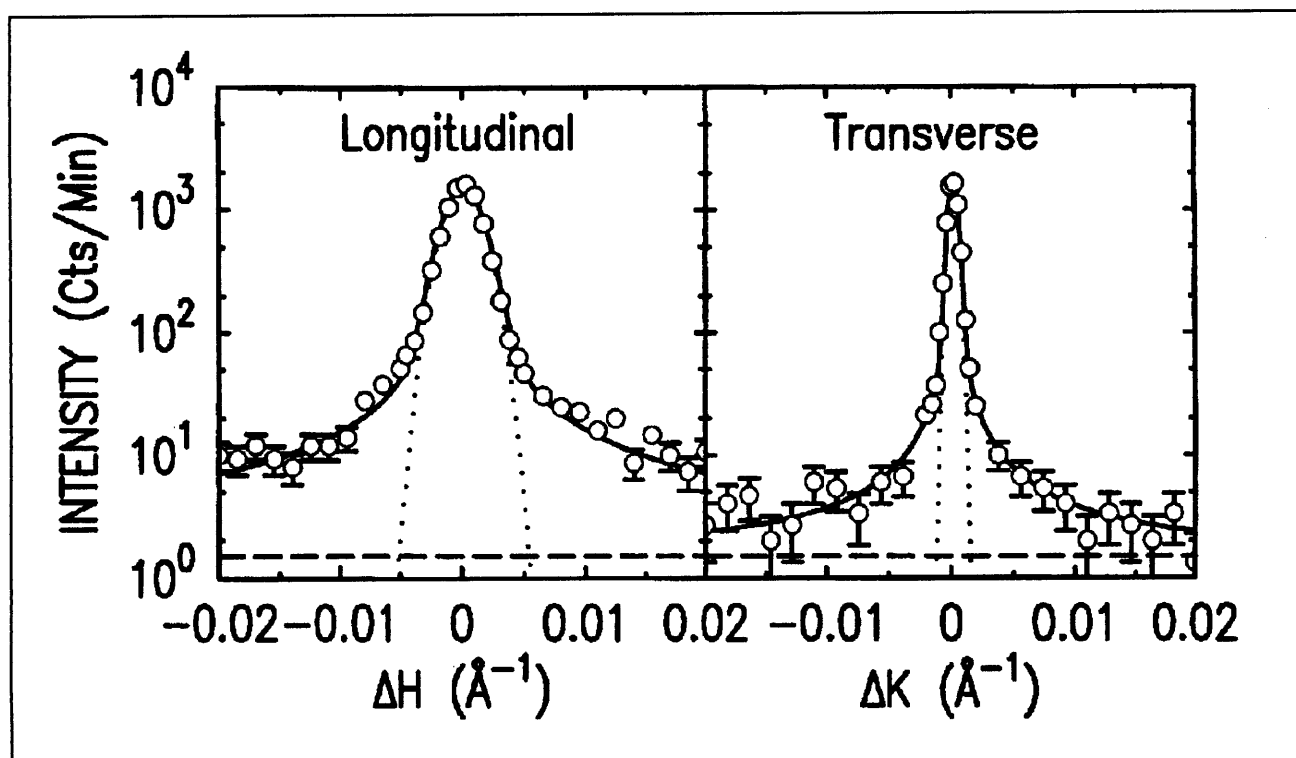


Figure 1. Longitudinal and transverse scans through the first order Si(111) step surface peak. The dotted curves are the resolution. The solid curves are the result of fits to the power-law lineshape with $\eta = 0.6$ and $B = 15$.



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