Chapter 2. Synchrotron X-Ray Studies of Surface Disordering

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2.1 Introduction

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, $\sim 1\text{Å}$, up to 30,000Å. 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 at Brookhaven National Laboratory, in collaboration with IBM, we have three fully instrumented beam lines. Two of these beam lines allow 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 have determined that a new chamber allowing access to a wider range of reciprocal space is required. In collaboration with Professor Simon G.J. Mochrie, we have designed, and are currently constructing, 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 temperature. 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

Previously, we carried out a detailed synchrotron x-ray study of the surface phases and phase transitions of a Au(110) surface. This specific Au(110) crystal had as its stable structure a 1×3 missing-row reconstruction. This corresponds to a periodic array of 4-atom wide (111) microfacets. The transition from this 1×3 structure to a 1×1 structure at 760 K involved a simultaneous deconstruction and roughening.

After further treatment of this same Au crystal we were able to obtain a stable 1×2 phase on the (110) surface. This latter phase is the one most commonly observed in previous experiments. The 1×2 structure corresponds to a periodic array of 3-atom wide (111) microfacets. There are subtle distortions at these faces of the atoms away from their bulk positions. We have performed a synchrotron x-ray scattering study of the thermal disordering of this Au(110) 1×2 reconstructed surface. Observing the temperature dependence of the in-plane superlattice and integral order surface peaks, as well as the $(\ell\ \ell\ 0)$ specular reflectivity,

we find that at Tc = 735 K the 1 × 2 surface undergoes a reversible deconstruction transition characterized by a proliferation of compact anti-phase defects with no measurable change in the density of surface steps. This transition is described by critical exponents close to those characterizing a two-dimensional Ising transition. We also find that by 784 K there has been a significant increase in the density of surface steps of the type associated with surface roughening. This suggests that the Au(110) surface disorders in a two step process, deconstruction followed by roughening, with a difference in the two transition temperatures of less than 50 K. This contrasts with the behavior we previously found for Au(110) 1 × 3 and which has been found recently by Robinson and coworkers[1] in Pt(110).

2.3 Semiconductor Surface Studies

2.3.1 Ge(111)

Currently, experimental information on the morphology of semiconductor surfaces near the bulk melting point is very limited, in spite of its evident importance in many growth processes. The Ge(111) surface has been reported to undergo a phase transition at a crystal temperature of about 1050 K, which is 160 K below the bulk melting temperature Tm (1210 K). The nature of the transition remains controversial.

At room temperature, a c(2 × 8) structure on the Ge(111) surface is stable. Near 573 K, the c(2 × 8) reconstruction converts to a (1 × 1) phase. The (1 × 1) structure may not have an ideally terminated bulk structure; adatoms are believed to be present. At higher temperatures a second structural transition of the Ge(111) surface was first suggested by Lever in 1968.[2] He found that the sticking coefficient of oxygen on Ge(111) dropped precipitously with increasing crystal temperature near 1050 K. McRae and Malic recently studied this reported transition in a Low-Energy Electron Diffraction (LEED) experiment.[3] The intensity of the surface diffraction peaks decreased rapidly near

1050 K saturating at a low but non-zero value. The results were interpreted on the basis of a heuristic model in which the outermost double layer of the Ge(111) consists of incommensurate crystalline islands surrounded by a disordered sea. Electron Energy Loss Spectroscopy done on a Ge(111) single crystal surface, as well as on liquid and amorphous Ge overlayers, suggested that the high temperature disordered Ge(111) surface resembles an amorphous layer more than a liquid layer. Ion scattering indicated that above ~ 1050 K there are local departures of surface atoms from their equilibrium lattice positions.

We have studied the Ge(111) surface using synchrotron x-ray scattering techniques with a glancing angle scattering geometry. Representative scans through the (10) peak at a series of temperatures bracketing 1070 K are shown in figure 1. It is evident that well-defined sharp peaks are observed up to temperatures near bulk melting; significantly, there is no important change in lineshape throughout this temperature range. Similar data are obtained for the (20) peak. The (10) and (20) peak intensities decrease gradually with increasing temperature above ~ 900 K, go through pronounced minima at about 1070 K and then partially recover.

From these data one may exclude all existing models for the surface disordering of Ge(111). We have, however, been able to show that a model involving surface vacancies gives a unique description of our data and is consistent with previous results. Specifically, we hypothesize that near 1000 K, thermally-generated random vacancies in the surface bilayer begin to proliferate. From a quantitative analysis we find that the surface vacancy concentration rises rapidly between ~ 950 K and 1080 K and then saturates; the limiting vacancy concentration is near 50 percent. We are also able to demonstrate that the vacancy concentration decays rapidly to the interior layers.

One important consequence of the high surface vacancy concentration is a dramatic growth in the rate of sublimation. So far there is little quantitative information on sublimation from defected surfaces. We plan to study this problem in more detail in the future.

[1] I.K. Robinson, E. Vlieg, and K. Kern. *Phys. Rev. Lett.* 63: 2578 (1989).

[2] R.F. Lever, *Surf. Sci.* 9: 370 (1968).

[3] E.R. McRae and R.A. Malic, *Phys. Rev. Lett.* 58: 1437 (1987); *Phys. Rev. B* 38: 13163 (1988).
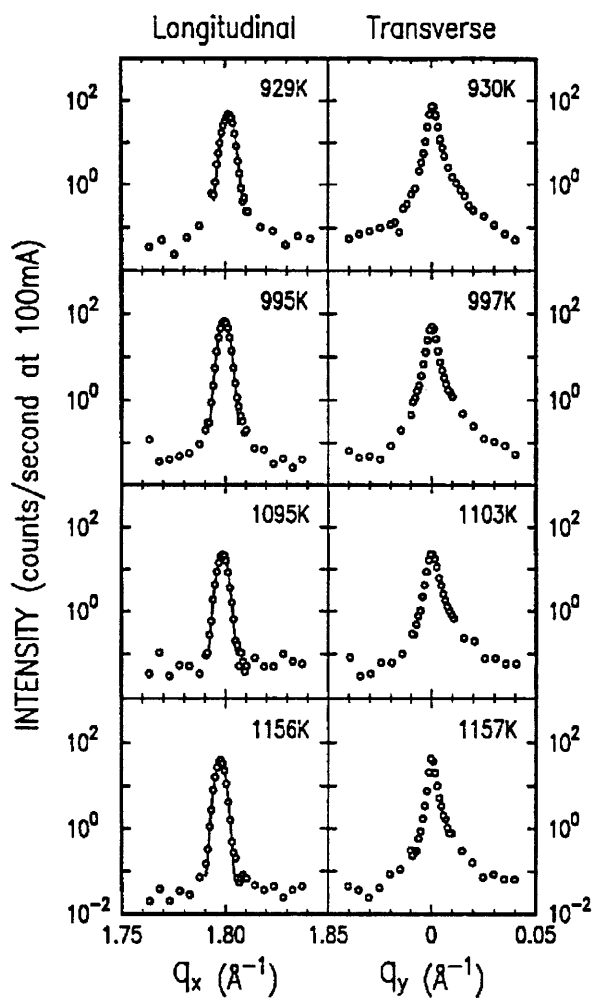
Figure 1. Longitudinal and transverse scans through the (10) peak are shown for four different temperatures: 929 K, 995 K, 1095 K, and 1156 K. The central portion of each of the longitudinal scans is fit to a Gaussian curve. All widths fall within $\pm 10\%$ of the instrumental width of $0.0022\text{\AA}^{-1}$ HWHM.

2.4 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 mechanism such as reconstruction. One might expect that the lowering of the 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 preliminary synchrotron x-ray scattering study of a vicinal Si(111) surface misoriented by 3.5° toward the (11$\bar{2}$) direction. At temperatures higher than the 7×7- to -1×1 transition, we find that the surface is composed of steps with a mean separation of $\sim 60\text{\AA}$ which are correlated beyond $3000\text{\AA}$. Below the transition, the surface is split into 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 7×7 reconstruction of the (111) facets. We are currently analyzing these data in terms of the equilibrium crystal shape of Silicon. We also have discovered other faceting configurations with higher indices which are presumably stabilized by impurities.

Both future experiments and future theoretical analysis are planned on this important problem.

2.5 Publications

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 × 2 Reconstructed Surface." *Surface Sci.* Forthcoming.

Mak, A., K. Evans-Lutterodt, K. 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." Submitted to *Phys. Rev. Lett.*
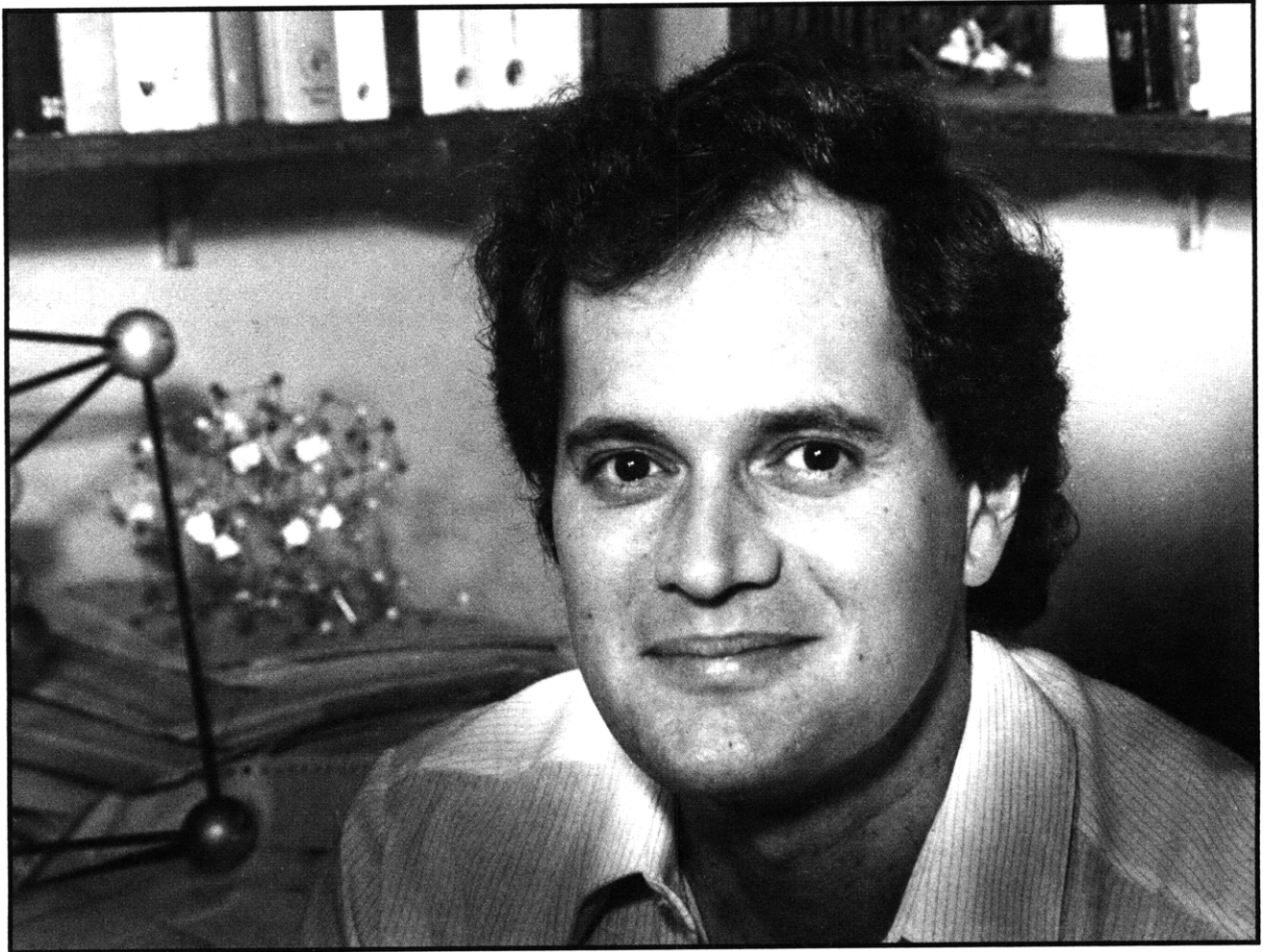
Theoretical studies conducted by Professor John D. Joannopoulos have provided many of the first ab-initio calculations for the electronic and geometric structure of solids.