Chapter 2. X-Ray Diffuse Scattering

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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, $\sim 1\text{Å}$, up to 30,000 Å. 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, we have, in collaboration with IBM, 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 18 keV. These facilities make possible high resolution scattering experiments with a flux more than three orders of magnitude larger than that from a rotating anode x-ray generator, opening up a new generation of experiments.

As part of this JSEP program, we have built an x-ray compatible high vacuum single crystal apparatus. This enables us to use synchrotron radiation to study the structures and transitions occuring at a single surface, and, indeed, such experiments are now becoming routine. Our current experiments in this program are concentrated on the phases and phase transitions of metal and semiconductor surfaces and surface overlayers.

2.2 Metal Surface Studies

We have carried out detailed studies of the reconstruction of the (110) surface of gold: Au(110). Many noble metal facets are known to favor reconstructed structures at low temperatures. Further, at some temperature T_c a reconstructed surface will typically undergo a reversible "deconstruction" to a high temperature structure which is no longer reconstructed. One such transition which has been studied theoretically as well as with electron diffraction is the Au(110) 1×2 to 1×1 deconstruction. While the "missing row" model of the reconstructed 1×2 surface is well established, the nature of the deconstruction transition itself remains controversial.

Previous work by our group has demonstrated that x-ray scattering is an effective means of studying surface phase transitions. Specifically, the lineshapes of bulk-forbidden surface peaks provide information about the surface height-height (or step-step) correlation functions and are thus a sensitive probe of the surface roughening transition. This transition is characterized by a proliferation of atomic steps which results in logarithmically divergent height fluctuations of the crystalline surface. We have carried out

glancing angle synchrotron x-ray scattering experiments as a means of studying the Au(110) structures and deconstruction transition. The results have been quite remarkable. The so-called 2 x 1 "missing row" model discussed above is a special case of a more general model in which one has (111) microfacets on the Au(110) surface. More extended microfacets can lead to reconstructions with longer periods: 1 x 3, 1 x 4, 1 x 5, etc., and these are very close in energy to the 1 x 2.

In our first set of experiments, the stable phase of the specific Au(110) surface turned out to be 1 x 3 rather than 1 x 2. The basic structure and the possible step excitations are shown in figure 1. For this structure superlattice peaks occur at $(0\ 0\ \ell/3)$ positions. We find that at 485°C the surface undergoes a continuous, reversible transition. At this transition the 1 x 3 long range order is lost and the local period becomes incommensurate. This behavior results from the proliferation of atomic steps (such as those shown in figure 1b and 1c), which act as domain walls between coherent regions of the reconstructed surface. In fact, by further studies we can determine that both types of steps are present. This means that the 1 x 3 surface both deconstructs and roughens simultaneously.

After further treatment of this same Au crystal, we were able to obtain a stable 1 x 2 phase on the (110) surface. This latter structure is the one most commonly observed in previous experiments. The deconstructive transition of this surface appears to be fundamentally different from that of the 1 x 3 phase. First, the structure remains commensurate even in the disordered phase. Second, there is no evidence of roughening. Third, we have some indication of 2D Ising critical behavior. Further analysis and measurements are required to elucidate the 1 x 2 deconstruction fully.

2.3 Semiconductor Surface Studies

We have investigated the surface disordering transition of Ge (111) near the bulk melting point. The experiment was performed at the National Synchrotron Light Source beamline X20A during the summer of 1989. Our observation was made on Ge wafers resistively heated inside a surface chamber which has a base pressure of 1.3×10^{-10} torr. The sample surface was prepared by sputtering for 30 minutes and subsequent annealing at the same temperature for one hour. Auger-electron spectroscopy was done in situ to check the surface cleanliness. The sample and surface chamber were oriented such that the in-plane (i.e., grazing incidence) (10) and (20) surface peaks, as well as the (11) bulk peak, were observable.

We have studied the evolution of the (10) and (20) surface peaks between 700 K and 1170 K, finding radical changes in intensity. The surface peaks remain resolution limited
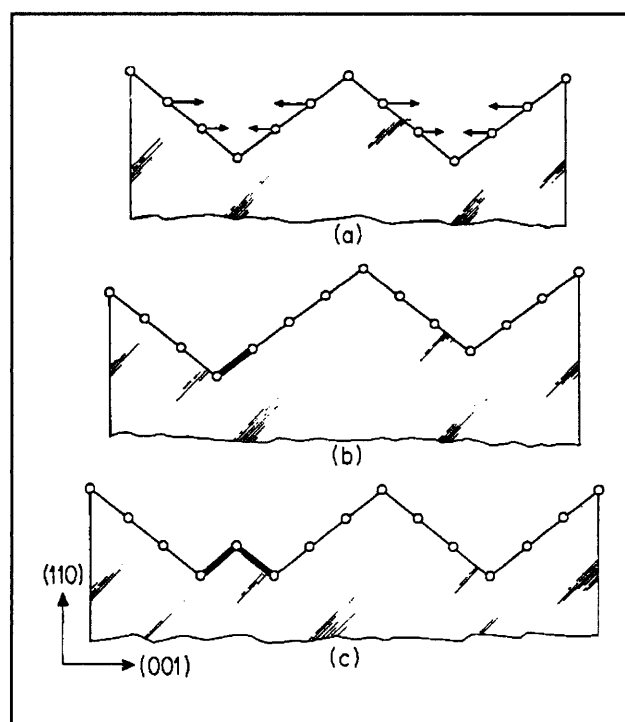

Figure 1. (a) Schematic representation of the Au(110) 1 x 3 missing-row reconstruction. The arrows indicate the southward atomic distrotions observed in the second and third rows from the surface. (b) A single atomic step thermal excitation of the 1 x 3 surface. (c) A paried-step thermal excitation of the 1 x 3 surface.

in the radial direction and the transverse widths stay the same throughout the entire temperature range. As the temperature goes up from 700 K, the intensity of the (10) surface peak decreases exponentially with a Debye-Waller factor of 0.001 K^{-1}. At about 1000 K the rate of decrease of the (10) peak intensity per degree K intensifies. The peak intensity goes through a minimum at about 1100 K and then recovers partially. The transition shown here is reversible with temperature, indicating that it is indeed an equilibrium phase transition. Similar behavior is observed for the (20) surface peak. We have also looked for signs of a surface fluid layer which should manifest itself as a broad ring in reciprocal space, but found no indication of such a layer. Subsequent to the x-ray scattering experiment, we have performed mass spectroscopy measurement on some Ge(111) samples. Each sample was placed one inch away from and with the normal pointing towards the probe. Our data show that there is an exodus of Ge atoms from the surface starting at about 1050 K.

None of the existing models of surface disordering — surface roughening and surface melting — can explain the data. The partial recovery of the surface peak intensity at about 100 K below bulk melting is particularly intriguing. We propose a model which would give a surface peak intensity that is consistent with our observation. A Ge crystal with an ideally terminated (111) surface consists of bilayers of atoms, stacked in an ..ABCABC.. sequence. The structure factor is identically zero at the surface peak position in reciprocal space because the scattering from every three bilayers of atoms exactly cancel. However, the penetration depth of x-rays in the direction normal to the surface is drastically reduced at grazing incidence, due to absorption and total internal reflection. The magnitude of the wave amplitude caused by a layer is maximum at the surface, dropping quickly as one moves into the bulk. As a result the sum of wave amplitudes from every three bilayers is nonzero: the amplitude from the top layers dominates that from below. Suppose that at 1000 K atoms on the sample surface pop-out randomly, leaving vacant sites behind. This reduces the amplitude from the top layer of

atoms. The net scattering intensity from the top three bilayers of Ge atoms reduces due to more effective cancellation. At 1100 K, the cancellation is optimized. At higher temperature, the random vacancy at the surface layer may be so large that the amplitude from the bottom layers now dominates. Since intensity is proportional to the modulus squared of the total wave amplitude from every layer, the intensity starts to increase once the random vacancy exceeds some critical value. In this model there is no broadening of the surface peaks, which is consistent with our observation. The mass spectroscopy measurement also supports this picture. Of course, this model is by no means unique. Further studies are required.

2.4 Rare Gases in Graphite

We have studied the phases and the phase transitions for a xenon solid layer on graphite in the monolayer coverage regime. The incommensurate solid undergoes the sequence of transitions: aligned → rotated → reentrant aligned, before the solid transforms into the commensurate solid. The current theory of orientational epitaxy correctly predicts only the point at which the rotation to the reentrant aligned phases occurs. None of the current theories can explain the whole picture of orientational epitaxy. Neither the high temperature aligned solid nor the reduction of the rotation angle from that of the static prediction are explained.

The reentrant aligned phase at low temperatures is an incommensurate solid with a network of superlight domain walls. The observed first-order phase transition can be explained within the domain-wall theory. The incommensurability at constant coverage decreases approximately as $[(T - T_0)/T_0]^{1/3}$ until the first order C-IC transition point is hit. This one-third power law is close to the behavior seen for Kr on graphite following a similar thermodynamic pathway.

We estimated the potential corrugation of the surface adsorption from the intensity ratios between the main and satellite peaks in the domain-wall incommensurate phase. The corrugation of the potential estimated was near the one predicted by Steele. Along with the estimation from the onset of the rotated

phase, we set the limits for the dimensionless wall width, $36 < \ell_0 < 42$.

At low temperatures the xenon layer on vermicular graphite did not transform into the commensurate phase as on the single-crystal substrate. Instead, the xenon layer seems to have a pinned domain-wall network due to defects.

2.5 Publications

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