Chapter 5. Step Structures and Epitaxy on Semiconductor Surfaces

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5.1 Project Description

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In this program, our goal is to obtain a detailed, experimental description of the temperature-dependent structure, phase-behavior, and morphology of semiconductor, especially silicon, surfaces. The results obtained in this way will be essential to theoretical efforts aimed at understanding silicon surface energetics. To this end, we employ high-resolution x-ray scattering, using an ultra-high-vacuum (UHV) apparatus for surface x-ray diffraction,[1] which was funded in-part by JSEP. The apparatus is located at the National Synchrotron Light Source (NSLS) and may be employed either at the MIT-IBM bending-magnet beamline, X20, or at the NSLS X25 wiggler beamline, which provides a five-fold intensity improvement compared to X20. The MIT UHV apparatus, in combination with either X20 or X25, constitutes the world's premier facility for surface x-ray scattering. In 1993, we continued to exploit its unique capabilities.

Specifically we have completed a comprehensive x-ray scattering study of the structure of the Si(113) surface. Current crystallographic techniques make it possible to determine the full three-dimensional atomic structure of a surface, with accuracies approaching 0.01 Å. Knowledge of the atomic structure is critical for evaluating calculations of surface energetics. It is surprising that the Si(113) surface has received much less attention up to now than the Si(001) and (111) surfaces. Nevertheless, the Si(113) surface is particularly interesting for a number of reasons which involve both possible technological applications and the basic physics of surfaces.

First, although Si(113) is a relatively high-index surface, it has been found to be remarkably stable with a surface energy comparable to that of the (111) or (001) orientation. Specifically, recent measurements of the shape of voids, created by He-ion implantation inside a Si crystal, have established that the surface energy of Si(113) is less than 1 percent higher than that of the Si(001) surface.[2] Understanding the geometric and electronic structure of such a low energy silicon surface is an important challenge in surface physics. Reports of superior epitaxial growth on Si(113)[3] make the structure of this surface and its temperature dependence especially worthy of study.

The rationale that Si(113) may be particularly suitable as substrate for epitaxial growth of III-V semiconductor films follows: An unreconstructed (113) surface may be envisaged as a sequence (001) terraces separated by (111) steps. For Si(113), the terraces are a single atomic row wide. The corresponding surface unit cell contains two different types of surface atoms: (a) two-fold coordinated atoms with two dangling bonds, deriving from the (001) terrace, and (b) three-fold coordinated atoms with a single dangling bond, from the (111) step (see figure 1a). Thus, there are two different adsorption sites. It seems likely that one of the sites will be preferred by one of the epitaxial

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1 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.

2 D.J. Eaglesham et al., "Equilibrium Shape of Si," *Phys. Rev. Lett.* 70: 1643 (1993).

3 G.H. Olsen, T.J. Zamerowski, and F.Z. Hawrylo, "Vapor Growth of InGaAs and InP on (100), (110), (111), (311), and (511) InP Substrates," *J. Cryst. Growth* 59: 654 (1982); S.L. Wright, M. Inada, and H. Kroemer, "Polar-on-nonpolar Epitaxy: Sublattice Ordering in the Nucleation and Growth of GaP on the Si(113) Surface," *J. Vac. Sci. Technol.* 21: 534 (1982).

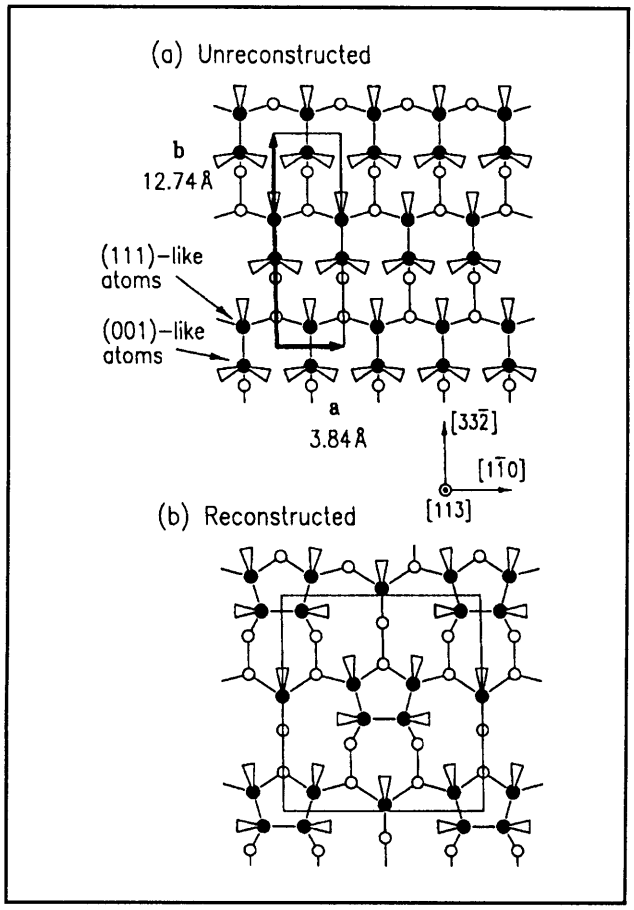

Figure 1. (a) Top view of unreconstructed Si(113) surface. The centered, unreconstructed unit cell is outlined. Silicon atoms in the surface layer are shown as solid circles. Atoms in lower layers are shown as open circles. Solid lines represent bonds between neighboring atoms while dangling bonds are shown as triangles. (b) Top view of Si(113) (3x1) reconstruction. The large box outlines the centered, reconstructed unit cell.

species, thus keying the growth film to the substrate in a definite manner. This feature may alleviate the problem of twinning that occurs in the growth of III-V semiconductors on flat Si(001),[4] which presently makes necessary the use of stepped Si(001) substrates for epitaxial growth. In addition, the (113) surface is non-polar, which avoids the possibility of strong disorder in the growth process as a result of electric fields. In fact, the clean Si(113) surface reconstructs to form a (3x1) structure. Our crystallographic measurements to determine the atomic positions at the Si(113) surface are described in section 2.[5] Our efforts in this regard are coordinated with those of Professor J.D. Joannopoulos, who is presently carrying out a total energy calculation of the Si(113) (3x1) structure.

In addition, we have initiated a study of the orientational phase diagram of stepped Si(113) surfaces between 300 and 1200 K. Stepped (or vicinal) Si(113) surfaces afford the opportunity to deepen our general understanding of the morphology of crystal surfaces. As described in detail in section 3, we have found that stepped Si(113) surfaces undergo a so-called facetting transformation. Facetting is accomplished through the rearrangement of surface steps, so that there are regions of the surface with a high step density, together with step-free Si(113) facets of macroscopic extent. We believe that the theoretical studies of the possible facetting of stepped Si(001) surfaces carried out by Professors A.N. Berker and J.D. Joannopoulos may lead to a detailed understanding of Si(113) facetting. Evidently, surface morphology is key to a number of technologically important processes, including epitaxial growth, etching, electromigration, and corrosion. An essential prerequisite for controlling these processes is an understanding of the equilibrium morphology of the surface. For example, our results demonstrate that large, step-free Si(113) surfaces may be prepared by high-temperature annealing. One may hope that the use of such surfaces as substrates for epitaxial growth might lead to interfaces of unprecedented perfection, which in turn may possess particularly favorable electronic transport properties.

5.2 The Structure of the (3x1) Reconstruction of the Si(113) Surface

X-ray diffraction measurements to determine the full three-dimensional atomic structure of the Si(113) surface at 800 K were performed at X20 using our UHV apparatus.[6] Our initial measurements were carried out in a glancing incidence geometry (in-plane measurements), so that the information gained concerned the atomic positions projected onto the surface plane. Relative structure factors at 130 surface Bragg reflections were collected, from which was derived the pair correlation function for atoms within the surface unit cell. The pair corre-

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4 K. Mizugachi et al., "MOCVD GaAs Growth on Ge(001) and Si(001) Substrates," *J. Cryst. Growth* 77: 509 (1986).

5 D.L. Abernathy, S. Song, K.I. Blum, 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; D.L. Abernathy, S. Song, K.I. Blum, and S.G.J. Mochrie, *Phys. Rev. B*, forthcoming.

lation function exhibits peaks corresponding to interatomic vectors, and therefore may be used to formulate structural models of the surface. Thus, our data indicate that the atomic structure is as shown in figure 1(b): the (3x1) structure is formed from the unreconstructed surface by removing every third (001)-like atom in the (1 -1 0)-direction, dimerizing the remaining two (001)-like atoms, and finally rebonding the (111)-like atom, neighboring the vacancy, to the layer below. Subsequent measurements at a large angle of incidence were carried out to be able to locate the atoms in the direction perpendicular to the surface. In total, approximately 600 intensities were collected, which reduce to 310 symmetry-inequivalent structure factors. Then, a full three-dimensional model of the reconstruction was least-mean-squares fit to the combined set of measured structure factors in order to refine the atomic positions. A comparison between the measured (open circles) and model (solid circles) in-plane structure factors is shown in figure 2, demonstrating excellent agreement. This work consitutes the first definitive determination of the (3x1) structure of the Si(113) surface.

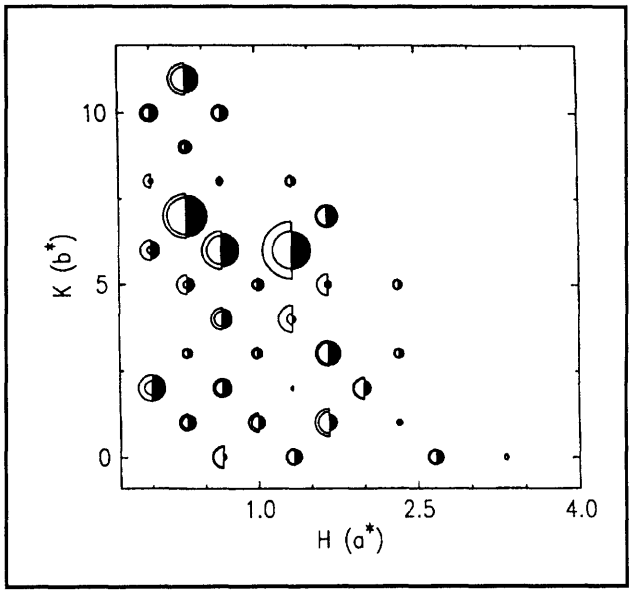

Figure 2. Comparison for Si(113) of the measured structure factors (open symbols) with calculations using the full three-dimensional model (solid symbols).

5.3 Morphology of Stepped Si(113) Surfaces

Equilibrium facetting is a remarkable phenomenon in which a crystal surface increases its area to decrease its free energy. Facetting is accomplished through the rearrangement of surface steps, so that their distribution across the surface is no longer uniform. Instead, there are macroscopic regions of high and low step density. Our present understanding of equilibrium facetting is based upon a description of the surface free energy in which the surface orientation is a key thermodynamic variable in addition to the temperature. In this context, facetting is an example of thermodynamic coexistence among different phases with different orientations. Moreover, such a description motivates the construction of orientational phase diagrams, within which are recorded the phase boundaries between different surface phases as the temperature and surface orientation are varied.

Experiments carried out at X20A using our UHV apparatus reveal a complex phase diagram for silicon surfaces oriented between (113) and orientations tilted roughly 6 degrees away from (113) towards (001), as illustrated in figure 3.[7] In figure 3, solid lines indicate phase boundaries and dashed lines indicate triple points. (The solid circles correspond to surface orientations found experimentally for the sample used in this study.) Within the range of temperature and tilt angle investigated, we have found three distinct orientational phases. Below T_3 = 1130 K, phase separation into the (113) orientation and the (114) orientation, which lies 5.7 degrees away from (113) towards (001) occurs for surfaces with mean tilt angle lying between (113) and (114). The scattering lineshapes of the (113) and (114) surfaces indicate that both are atomically smooth facets in this temperature range. However, at T_3 there occurs a phase transformation at which the (114) facet disappears and are replaced by a surface with a tilt angle of 6.5 degrees. Our measurements indicate that for this phase the scattering lineshape becomes increasingly broad with increasing scattering angle, which is the behavior expected for a rough surface. Therefore, we believe that the 6.5 degree-tilted surface corresponds to a *rough phase.* All three phases, namely the (113) facet, the (114) facet, and the rough phase, may coexist at T_3, which thus is a triple point temperature. Above T_3, there is coexistence between the (113) facet and the rough phase. For temperatures increasing above T_3, the tilt angle of the rough surface decreases with increasing temperature while the intensity of the scattering from the (113) facet decreases. Eventually, at 1200 K, the tilt angle of the rough surface reaches the value determined by the macroscopic cut of the sample, which for the data shown in figure 3 was 3.8

[7] S. Song and S.G.J. Mochrie, *Phys. Rev. B*, forthcoming.

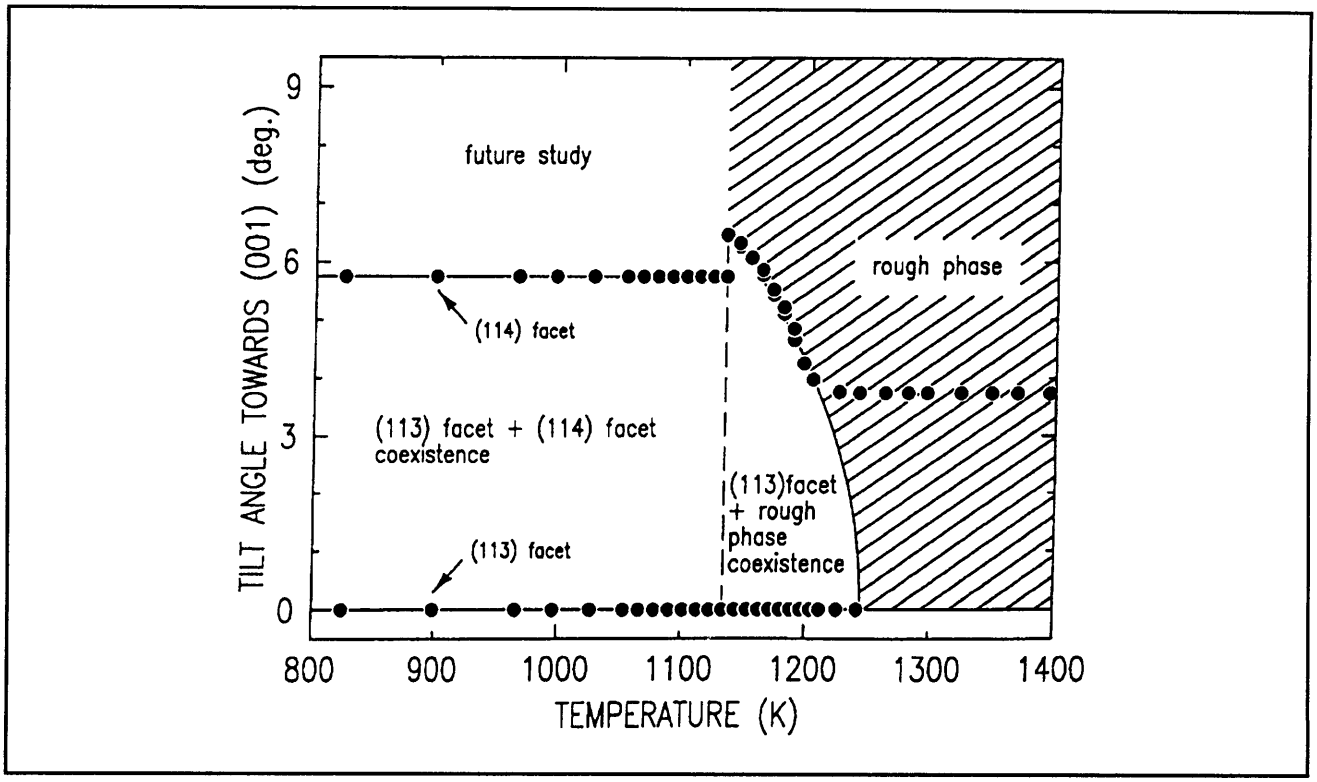

Figure 3. Orientational phase diagram of the Si surface near the (113) direction for tilt angles towards (001). Single-phase regions are hatched, and two phase regions are plain (unhatched). Solid lines are boundaries between two phases, and dashed lines represent triple points. Solid circles represent tilt angles measured for a sample with a mean tilt angle (miscut) of 3.8 degrees.

degrees, and the (113) facet essentially disappears. On further increase in the temperature, the tilt angle remains fixed because the surface lies in a one-phase region of the orientational phase diagram shown hatched in figure 3. We have extrapolated the boundary of the (113) facet-rough phase two-phase coexistence region to zero tilt angle at T_0 = 1245 K. The character of the transformation from (113) facet to rough phase at this point is presently undetermined. Future experiments will study the interesting possibility that it is a critical point.

5.4 Publications

Abernathy, D.L., D. Gibbs, G. Grübel, K.G. Huang, S.G.J. Mochrie, A.R. Sandy, and D.M. Zehner. "Reconstruction of the (111) and (001) Surfaces of Au and Pt: Thermal Behavior." *Surf. Sci.* 283: 260 (1993).

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

Abernathy, D.L., R.J. Birgeneau, K.I. Blum, and S.G.J. Mochrie. "Critical Behavior at Chiral Melting: Disordering of the Si(113) (3X1) Reconstruction." *Phys. Rev. Lett.* 71: 750 (1993).

Grübel, G., D. Gibbs, D.M. Zehner, D.L. Abernathy, A.R. Sandy, and S.G.J. Mochrie. "Phase Behavior of Au and Pt Surfaces." *Surf. Sci.* 287/288: 842 (1993).

Thesis

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