Dynamics of the Si(111) Surface Phase Transition

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Abstract

We have use low-energy electron microscopy to investigate the dynamics of the Si(111) 7 × 7 → 1 × 1 phase transition. Because the densities of the two phases differ, the phase transformation is analogous to precipitation in bulk systems: additional material must diffuse to the phase boundaries in order for the transformation to occur. By measuring the size evolution of an ensemble of domains, and comparing the results to simulations, we have identified a new mechanism of precipitate growth. The source of material necessary for the transformation is the random creation of atom/vacancy pairs at the surface. This mechanism contrasts sharply with classical theories of precipitation, in which mass transport kinetics determine the rate of transformation.

When the temperature of a material is varied, changes of phase can occur. Phase transformations are typically accompanied by changes in composition and density. The kinetic mechanisms involved in the phase transformation determine the structure of the material, and hence control many physical properties. Thus much effort has been devoted to understanding the kinetics
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of solid-solid phase transformations. The prototypical example is steel. The equilibrium structures of steel are characterized by varying concentrations of carbon. In order for a change of phase to occur (e.g. upon cooling from high temperature), carbon must either diffuse to or away from the favored domain. In the earliest quantitative analysis of precipitation, it was realized that the rate of precipitate growth is determined by the energetics of the diffusion process [1]. That is, precipitate growth is fundamentally limited by the rate at which carbon diffuses to or away from the precipitate particle.

In this paper we explore the kinetics of a phase transition by investigating a well-known phase transformation that occurs at the surface of a solid. Surface phase transitions involve changes in the arrangement of atoms at the outermost layers of a solid, but not the atoms within the bulk of the material. By confining the transition to the surface, we are able to follow the transformation in situ using modern surface microscopy techniques. Although the physical principles that govern surface phase transitions are the same as those in the bulk, we show that the presence of surface provides new mass transport mechanisms, leading to dynamics that cannot be described using classical theories of precipitate growth.

The phase transition we have investigated is the 7 x 7 to 1 x 1 structural transformation of the Si(111) surface. Using low-energy electron microscopy (LEEM) [2], we have measured the evolution of surface morphology during the transition. At temperatures above 1125 K, the surface undergoes a first-order [3, 4] phase transition from from the reconstructed 7 x 7 structure to an unreconstructed 1 x 1 -like phase [5, 6]. The low-temperature phase is a complicated reconstruction involving three surface layers [7]. The 1 x 1 structure consists of dense, disordered structure on top of the bulk-terminated surface [8]. The structural transformation in this system is qualitatively similar to bulk precipitation: the density of the 1 x 1 phase is 6% larger than that of the low-temperature 7 x 7 phase [9]. Conversion of the 7 x 7 structure to the 1 x 1 structure requires the incorporation of additional Si at the boundaries between the phases.

A central question is: where does this material come from? Reflection electron microscopy studies suggest that steps at the surface are the ultimate source of the additional Si required for the conversion to occur [10]. The conversion of 7 x 7 domains on the terrace reduces the density of thermally-generated atoms on the surface. The atom density is resupplied by the evaporation of Si atoms from step edges on to the terrace (Fig. 1a). As the phase transition proceeds, the steps retract 'uphill' as material is supplied to
the terrace. We find, however, that atoms do not directly migrate from step edges to the domain boundaries. We have identified an important intermediate process that completely determines how the domains evolve in time. Specifically, we find that the random creation of atom/vacancy pairs on the surface provides the additional Si required for the transition. The atoms diffuse to the domain boundaries, and the vacancies diffuse to the step edges, leading to the observed step retraction (Fig. 1b). The existence of this source of atoms shows up clearly in our measurements of how ensembles of domains evolve above the phase transition temperature, and leads to precipitate growth that is qualitatively different from precipitation observed in bulk systems. The essential difference is that the source of material required for the phase transition to proceed is continuously supplied to the surface. As we discuss below, diffusion of atoms at the surface is sufficiently fast that rate at which the surface precipitates decay is governed by the rate at which atoms are supplied to the surface. This new mechanism of precipitate growth is enabled because the activation energy associated with atom/vacancy creation at the surface is roughly half the bulk value.

A LEEM image from the Si(111) surface 10 K above the phase transition temperature is shown in Fig. 2. The image was formed from 10 eV electrons scattered specularly from the surface. The reflectivity of the 7 × 7 regions (for 10 eV electrons) is higher than that of the 1 × 1 regions. Consequently, the 7 × 7 regions appear bright in the LEEM images. The initial domain configuration was formed by rapidly cooling below the transition temperature following a flash to 1500 K to clean the surface. Upon cooling from high temperature, the 7 × 7 domains nucleate first at the upper side of step edges [3]. Isolated domains have domain boundaries in the ⟨112⟩ directions [11], and are usually triangular. In addition to isolated 7 × 7 domains, and 7 × 7 domains at step edges, domains of 1 × 1 structure completely surrounded by 7 × 7 regions are also observed (Fig. 2). Above the phase transition temperature, the structure shown in Fig. 2 is not stable. The fraction of the surface covered by the 7 × 7 structure decreases with time as the conversion to the 1 × 1 structure proceeds. The evolution of the domain structure is illustrated in the series of images shown in Fig. 3.

By measuring the time evolution of the domain sizes, the mechanisms of precipitation can be probed. In each frame of a sequence of images, the domain areas are determined by fitting each domain to a polygon. The time evolution of the areas of selected domains in Fig. 3 are shown in Fig. 4. Several conclusions can be made immediately from the data. First, there is a
striking variation in the measured decay rate among the domains. The variation suggests that the incorporation rate of atoms at the domain boundary is fast compared to surface diffusion. If the incorporation rate were small, gradients in the concentration of atoms on the surface would not develop. Every domain would be surrounded by the same atom density, and would decay at the same rate.

The most striking feature of the data in Fig. 4 is the fact that decay rate is independent of the domain size. The decay rate of an individual domain is essentially constant throughout the decay of the domain. Surprisingly, the decay rate is strongly correlated with the initial size of the domain. Domains that are large when the decay begins have larger decay rates throughout the decay. The decay rate is apparently determined by the local environment of the domain: the locations of neighboring domains and bounding step edges.

All of these features of the data are reproduced in detail by a mathematical model that assumes the random creation of atom/vacancy pairs at the surface. In the limit where the atom/vacancy creation rate is small compared to the hop rate of atoms and vacancies at the surface, the process can be modeled as a constant flux of atoms and vacancies onto the surface. The decay of isolated $7 \times 7$ domains is therefore analogous to the growth of two-dimensional islands from a flux [12, 13]. The diffusion equation governing the concentration of atoms at the surface, $c_a$, is given by:

$$D_a \nabla^2 c_a + R_1 - R_2 c_a c_v = 0,$$

where $R_1$ is the rate at which atoms and vacancies are created and $R_2$ is the probability that an atom and vacancy at the surface recombine. An identical equation governs the surface vacancy concentration, $c_v$. In this model the only source of Si is the atom/vacancy creation process. The quantities $R_1$ and $R_2$ define the equilibrium concentrations of atoms and vacancies at the surface, $\bar{c}_a$ and $\bar{c}_v$. In terms of these quantities, Eq. (1) becomes:

$$D_a \nabla^2 c_a + R_1 (1 - \frac{c_a c_v}{\bar{c}_a \bar{c}_v}) = 0.$$  

In the limit $c_a c_v \ll \bar{c}_a \bar{c}_v$, Eq. (2) reduces to the diffusion equation with a constant flux term equal to $R_1$. Physically, this limit is reached when the atomic hop rate at the surface is fast compared to the atom/vacancy creation rate.

We have used this model to analyze the domain decay shown in Fig. 4. We assume that atom diffusion is sufficiently fast that the atom/creation process
can be represented by a constant flux, \( F \), incident on the \( 1 \times 1 \) regions of the surface. From measurements of the evolution of \( 1 \times 1 \) domains completely surrounded by \( 7 \times 7 \) areas, described below, we conclude that atom/vacancy creation on \( 7 \times 7 \) regions of the surface can be neglected.

The decay rate of a domain is equal to the rate at which atoms reach the phase boundary from the terrace:

\[
\frac{dA}{dt} = \omega \int D_a \nabla c_a \cdot d\vec{l},
\]

where \( A \) is the area of the domain, \( \omega \) is the area of an atom, \( D_a \) is the surface diffusion constant for atoms. This model assumes that the domain boundaries are perfect sinks for the diffusing atoms [14]. The atom concentration on the terrace is determined by solving the diffusion equation for atoms:

\[
D_a \nabla^2 c_a + F = 0,
\]

where \( F \) is a uniform, time-independent flux of atoms onto the surface. The boundary condition is that the atom concentration vanishes at domain boundaries [15]. It is clear from Eq. (4) that the concentration on the terrace is proportional to \( F/D_a \). Consequently, the decay rate of a domain (Eq. 3) will be equal to a characteristic rate \( \omega F \) multiplied by a geometric factor independent of \( D_a \). The only free parameter in this model is the flux, which determines the overall time scale of the decay. In addition, the relative decay rates of the domains are determined solely by the initial configurations of domains and cannot be adjusted. In the simulations Eq. (2) is solved for the initial configuration of domains. The decay rate of each domain is determined from Eq. (3). The domain sizes are adjusted based on the computed decay rates. The diffusion equation is then solved for the new configuration, and the process is repeated to generate the area-versus-time curve for each domain. During the decay, the shape of each domain in the simulation is fixed. A comparison between the measured and simulated domain decay is shown in Fig. 4. The best agreement between simulation and experiment corresponds to \( \omega F = 1.04 \times 10^{-4} \) monolayers (ML) per second [16]. Assuming reasonable values for the prefactor, this rate corresponds to an activation energy for atom/vacancy generation in the range 3.2 to 3.8 eV. The model clearly reproduces both the constant decay rate of individual domains as well as the observed variation in the decay rates among the domains. The value of the flux can also be estimated from the data in Fig. 4. The initial coverage
tion energy of this process determines the time scale of the phase transition. This behavior contrasts sharply with precipitation in bulk systems, which is governed by the energetics of mass transport. The deviation from bulk-like dynamics is due to the unique hierarchy of energy barriers at the surface. Specifically, the activation energy associated with atom/vacancy creation at the surface is about half the value corresponding to interstitial/vacancy creation in the bulk ($\sim 6 \text{ eV}$ [17]), enabling a new mechanism of precipitation. On the basis of simple bond counting, a lower atom/vacancy creation energy at surfaces compared to the bulk should be common. As this work shows, reduced barriers at surfaces can lead to morphological evolution that is qualitatively different from that of the bulk.

References


[14] This simplifying assumption is motivated by the observation that all 7×7 domains decay in the range of temperatures we investigated. Ostwald ripening, where large domains grow (or decay more slowly) than small domains is not observed.

[15] To simplify the computation, 7 × 7 domains at step edges are treated as fixed boundary conditions which do not change in time. Only the evolution of isolated domains on the terrace is considered.

[16] This value reflects the density difference between the 7 × 7 and 1 × 1 structures. Only 6% of a monolayer of additional Si is required to convert the entire surface from the 7 × 7 to the 1 × 1 structure. One monolayer is defined as the density of atoms in the ideal, bulk-terminated surface.

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Figure 1: Processes leading to $7 \times 7$ domain decay and step retraction. (a) atoms evaporate from step edges and incorporate at phase boundaries. (b) Random atom/vacancy creation on the surface produces atoms that diffuse to phase boundaries, and vacancies that annihilate at step edges.
Figure 2: Bright-field 10 eV LEEM image of the Si(111) surface at 1130 K with $7 \times 7$ and $1 \times 1$ domains. Dark arrows indicate step positions. A $1 \times 1$ domain completely surrounded by the $7 \times 7$ structure is indicated by a white arrow. The length of the scale bar is 1 $\mu$m.
Figure 3: Sequence of bright-field 10 eV LEEM images of the Si(111) surface at 1135 K. The time interval between images is 50 s. Step edges run horizontally near the top and bottom of each frame. The length of the scale bar is 1 µm.
Figure 4: Decay rates for selected $7 \times 7$ domains. (a) Marked domains from Fig. 3(d). The length of the scale bar is 1.0 μm. (b) Circles indicate measured domain areas. Solid lines are the simulated decay curves using the model described in the text with $F = 1.0 \times 10^{-4}$ ML/s.
Figure 5: Growth of $1 \times 1$ domains above the phase transition temperature. 
(a) Bright-field 10 eV LEEM image of $1 \times 1$ domains surrounded by $7 \times 7$ regions at 1140 K. The length of the scale bar is 1.0 μm (b) Areas of the indicated domains as a function of time. Light lines are the measured areas. Solid lines are the simulated areas with $F = 1.6 \times 10^{-4}$ ML/s.