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Structural fluctuation of dimers on Ge(001) surface near transition temperature

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Abstract

The structural fluctuation of the orientational arrangement of buckled dimers on a Ge(001) surface near the transition temperature of the order–disorder phase transition is investigated by time-resolving dynamical Monte Carlo simulations. STM images averaged in a finite period are derived from the simulation. The coexistence of the c(4 × 2) and the apparent (2 × 1) domains in the STM images observed by experiments is reproduced in the simulated STM images. We show that the coexistence on the Ge(001) surface can be attributed to the critical slowing down near the transition temperature.

Keywords: Monte Carlo simulation; Scanning tunneling microscopy; Germanium; Phase transition; Surface thermodynamics; Critical slowing down; Self-similarity

1. Introduction

Intensive studies have been made on the atomic structures of a Ge(001) surface and a Si(001) surface, where the neighboring surface atoms form dimers. Each dimer buckles and takes an asymmetric structure. The buckled dimers have two stable tilting angles depending on their respective local configurations. The orientational arrangement of the buckled dimers orders into the c(4 × 2) structure through the order–disorder phase transition on the Ge(001) surface [1–7]. At low temperatures, most of the dimers, except those near the structural defects, are observed as the asymmetric images by the scanning tunneling microscopy (STM). The asymmetric images observed by STM result from the asymmetry structure of the dimers. At temperatures above the transition temperature, the dimers are observed by STM as apparent symmetric images [3], which have been attributed to the rapid flip–flop motion of the buckled dimers during STM scanning. The symmetric images of the buckled dimer on the Si(001) surface and the Ge(001) surface observed by STM have been referred to as the symmetric-appearing images [7–12].

First-principles calculations (FPC) [4,5] show that the relative energy differences between optimized structures on the Ge(001) surface are almost same as those on the Si(001) surface. However, the heights of the energy barrier for the flip–flop motion on the Ge(001) surface are about 120 meV larger those that on the Si(001) surface [4,5,7,13]. The long-time-averaged thermal equilibrium properties on the Ge(001) surface are similar to those on the Si(001) surface, but the time scale of the thermal fluctuations on the Ge(001) surface is much larger than that on the Si(001) surface. At very low temperatures, the quantum excitation of the dimer vibration by the tunneling current of STM is dominant for the structural fluctuation on the Si(001) surface and the Ge(001) surface [8,14,15]. The temperature of the order–disorder phase transition (T_c) on the Ge(001) surface is derived to be about 315 K from the results of Monte Carlo simulations (MCS) [4,5] with the Metropolis algorithm based on the results of

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FPC [4,5] by mapping the two stable orientations of the dimer onto the Ising system. The results of MCS [6] on the Ge(0 0 1) surface with low defect density reproduce well the feature of the temperature dependence of the X-ray diffraction intensity [2] on the Ge(0 0 1) surface.

Time-resolving dynamical Monte Carlo simulations (TDMCS) [7] have been performed for the time-fluctuating orientational arrangement of the dimers on the Ge(0 0 1) surface at 200 K. The heights of the energy barriers for the flip–flop motions of the dimers for TDMCS are obtained with the model potential [7] for the continuous values of the tilting angles of the dimers based on the results of FPC [4,5]. The results from TDMCS [7] reproduce well the observed results from the time-resolving constant-height current mode STM (TCHC STM) [3]. FPC [4,5] and the model potential [7] for the Ge(0 0 1) surface are shown to be sufficiently accurate to investigate the properties of the time-fluctuation as well as the long-time-averaged thermal equilibrium properties.

At temperatures near the transition temperature (T_c), the coexistence of the c(4 × 2) and the apparent (2 × 1) domains in the STM images have been reported on the clean Ge(0 0 1) surface [16–18]. The dimer images in the apparent (2 × 1) domains are observed as the symmetric-appearing images in STM, while those in the c(4 × 2) domains are seen as the asymmetric images. These domains form striped patterns whose width typically extends to 10 dimer rows. The coexistence was attributed to the long range anisotropic surface stress on the Ge(0 0 1) surface [16–18].

In the present study, we perform TDMCS for a clean Ge(0 0 1) dimer system near T_c to investigate the structural fluctuation of the orientational arrangement of the buckled dimers on the Ge(0 0 1) surface near T_c. STM images with a finite observation period are derived from the results of TDMCS. We shall see that the striped patterns are reproduced without the long range surface stress.

2. Time-resolving dynamical Monte Carlo simulations

In the present study, the structural fluctuation of the orientational arrangements of the buckled dimers on the Ge(0 0 1) surface near T_c are investigated by TDMCS. We use the same method for TDMCS as used on a Ge(0 0 1) surface at 200 K [7] and a Si(0 0 1) surface [9,13]. The method is essentially the same as that employed by Maksym [19] and Kawamura [20]. TDMCS requires the kinetic transition rate of the flip–flop motion from one of the stable angles to the other. The transition rate γ_k for kth dimer at temperature T is represented by the theory of absolute reaction rates as $\gamma_k = A\exp(-W_k/k_BT)$, where A is the attempt frequency. The value of A is obtained approximately as $A = 3$ THz for the dimer system of the Ge(0 0 1) surface by comparison of the results of TDMCS [7] and TCHC STM [3]. W_k is the height of the energy barrier for the flip–flop motion of the kth dimer. The heights of the energy depend on the respective local configurations of the dimers. We obtained values of W_k using the model potential [7] for the continuous values of the tilting angles of the dimers based on the results of FPC [4,5]. The model potential [7] and the Ising Hamiltonian [4,5] consist of short range couplings between the dimers, not any long-range couplings. In both, couplings have the short-range anisotropy: the coupling constants along the dimer row are much larger than those perpendicular to the row. Because of this short range anisotropy, the dimer arrangements mostly fluctuate along the dimer row. Most long range fluctuations are carried by the phase boundary in the dimer row [7,10–13,21,22].

We employ a system consisting of 512 dimer rows where each row consists of 2048 dimers. The periodic boundary conditions are assumed for both perpendicular to and along the dimer row. T_c derived from the MCS depends slightly on the system size employed. From MCS in the smaller system, T_c is estimated to be about 315 K [4–6]. In the present system, T_c is obtained as about 312 K which is derived from the temperature dependence of the long-range order parameter of the c(4 × 2) structure by MCS with the Metropolis algorithm. In the present study, TDMCS is performed at 314 K to investigate the structural fluctuation near T_c. As the temperature decreases closer to T_c, the correlation length and the time constant of the structural fluctuation become longer; both then diverge at T_c. The system size used in the present study is large enough for MCS at 314 K. The larger system for MCS is required to investigate the structural fluctuation on the Ge(0 0 1) surface at lower temperatures. In our computational system, it is difficult to perform MCS at temperatures lower than 314 K.

The initial configuration for the TDMCS at $t = 0$ is prepared by MCS with the Metropolis algorithm [4,5], where t is the time in TDMCS. The initial configuration of the system at 314 K is shown in Fig. 1 where the site (i,j) is at the jth dimer on the ith dimer row. The $c(4 \times 2)$ structure has the two energetically equivalent phases. The phase $P_{i,j}$ is defined as $P_{i,j} = (-1)^{i+j}\,\mathrm{sign}(\theta_{i,j})$, where $\theta_{i,j}$ is the tilting angle of the dimer at the site (i,j) and $\mathrm{sign}(x)$ is defined as $\mathrm{sign}(x) = 1, -1$ for $x \geqslant 0$ and $x < 0$, respectively. Sites with phases of $P_{i,j} = 1$ and $P_{i,j} = -1$ are assigned to with red and blue [1] in Fig. 1, respectively. In Fig. 1, the self-similar two-dimensional pattern which is well known to appear near the transition temperature of the second-order phase transition, is seen.

The configuration of the dimer system started from the initial one fluctuates with time, and the STM images of the dimers observed in the experiments correspond to the time-averaged configuration of the dimer. The regions on the Ge(0 0 1) surface fluctuating fast enough to show the symmetric-appearing images within the period of the STM observation of the respective dimers are assigned to

[1] For interpretation of color in Figs. 1,2,3,4, readers is referred to the web version of this article.