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Roughening and Preroughening of Diamond-Cubic {111} Surfaces

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A solid-on-solid model for {111} surfaces of diamond-cubic materials that correctly takes into account the diamond-cubic crystal structure has been developed for Monte Carlo simulation. In addition to a roughening transition at temperature T_R, a distinct preroughening transition at $T_{PR} \approx 0.43T_R$ is indicated by divergences in the surface specific heat and order-parameter susceptibility. Preroughening appears to arise naturally in our nearest-neighbor bond model from the entropic freedom available in the nontrivial crystal structure. Preroughening is shown to dramatically lower the nucleation barrier for growth and etching at low driving forces.   [S0031-9007(96)02096-0]

As temperature increases, a faceted crystal surface may undergo a disordering of its height profile in a series of phase transitions known as roughening and preroughening (PR). In conventional roughening [1], the free energy of steps on the surface vanishes at a critical temperature, T_R. On a microscopic scale the surface becomes rough as steps are spontaneously formed, while on a macroscopic scale the facet disappears from the equilibrium crystal shape. The PR transition was first described by Rommelse and den Nijs [2] as a transition from an ordered, flat surface to one called disordered flat (DOF) that is macroscopically flat but microscopically rough due to a proliferation of steps with long-range up-down order. Although it initially received attention in connection to surface reconstruction, PR has received much recent attention in the context of {111} surfaces of noble gases adsorbed on graphite substrates, where reconstruction is not expected to be a driving force for disordering [3,4].

In this Letter we present results of extensive Monte Carlo (MC) simulations investigating the roughness of {111} surfaces of silicon and other diamond-cubic (DC) materials. We predict for the first time a PR transition on these important surfaces. Contrasting most models considered to date, which use restricted solid-on-solid (RSOS) models and further than nearest-neighbor (NN) interactions, we find that both roughening and PR arise naturally in our model with only NN interactions due to the nontrivial crystal structure. We discuss our results in context with other simulations and recent experiments on silicon.

We have developed a solid-on-solid (SOS) model for {111} surfaces of DC crystals, details of which have been reported elsewhere [5,6]. The correct DC structure has been incorporated to ensure proper NN coordination, rotational symmetry, and layer-stacking periodicity along the [111] direction. SOS columns are arranged on a triangular net, and grouped into three sublattices, *A*, *B*, and *C* (Fig. 1), with the total number of columns given by $N = L \times L \times 3$. The column heights are restricted to conform to the DC structure. Standard Metropolis MC simulation has been implemented using periodic boundary conditions and NN interactions characterized by a bond energy J. The possible effects of reconstruction, known to be of importance on Si{111}, are not included in our model in order that we may concentrate only on the most fundamental effects of the crystal structure. Reconstructions on DC {111} surfaces are not expected to have a significant influence on fluctuations normal to the surface at high temperature T. Furthermore, the 7×7 reconstruction in Si{111} changes to 1×1 at high temperature [7], where we are most interested.

In order to identify the roughening transition temperature, T_R, we have examined the height-difference correlation function,

$$G(r) \equiv \langle [h(\mathbf{r}) - h(\mathbf{r}_0)]^2 \rangle, \qquad (1)$$

which is expected to diverge as

$$\lim_{r \to \infty} G(r)/a^2 \to [K_\infty(T)/\pi]\ln(r) \qquad (2)$$

for $T \geq T_R$. Here, $h(\mathbf{r})$ is the height of a column, $r = |\mathbf{r} - \mathbf{r}_0|$ is the lateral distance of a column to a reference column at $\mathbf{r}_0$, a is the surface-normal stacking period, and $\langle \ldots \rangle$ denotes thermal averaging. The prefactor in Eq. (2) takes on a universal value at T_R: $K_\infty(T_R) = 2/\pi$, and is a convenient aid in identifying T_R. Following
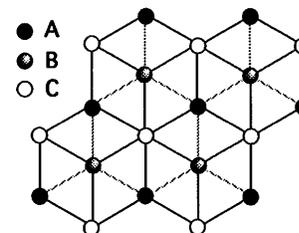

FIG. 1. Schematic DC crystal structure projected on (111). Circles represent SOS columns of atoms at heights allowed by the DC structure, and grouped according to *A*, *B*, and *C* sublattices.
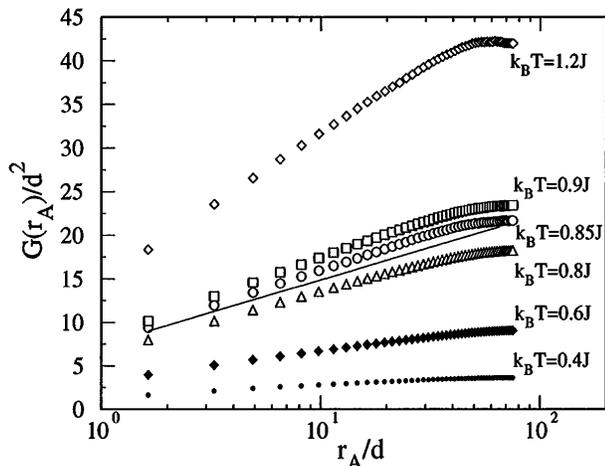
FIG. 2. Semilog plot of the height-difference correlation function, $G(r)/d^2$, versus the lateral column separation, r/d, where d is the nearest-neighbor bond length. Here, distances $r = r_A$ are taken between A-A column pairs only, although curves with $r = r_B$ and $r = r_C$ behave similarly [6]. The straight line has a slope of $16K_\infty(T_R)/\pi$. The factor of 16 arises from the DC {111} stacking periodicity $4d$. Results are averaged over 4×10^6 Monte Carlo sweep (MCS) after equilibration of at least 10^6 MCS for each temperature on a surface with $L = 93$.

Ref. [8], we identify $k_BT_R = 0.84 \pm 0.03J$ by locating the temperature at which $K(T)$ takes on the universal value from fits of $G(r)$ to Eq. (2) (see Fig. 2 and Ref. [6]).

The roughening transition near $k_BT_R = 0.84J$ is also evidenced by a rather broad peak in the surface specific heat (Fig. 3), calculated from fluctuations of the surface energy, E, according to

$$C(T) = \frac{1}{Nk_BT^2}\left(\langle E^2\rangle - \langle E\rangle^2\right). \quad (3)$$

Although no discontinuity or divergence is expected in $C(T)$ at $T = T_R$, the broad peak in the range $0.5J < k_BT < 1.0J$ is consistent with roughening [9].
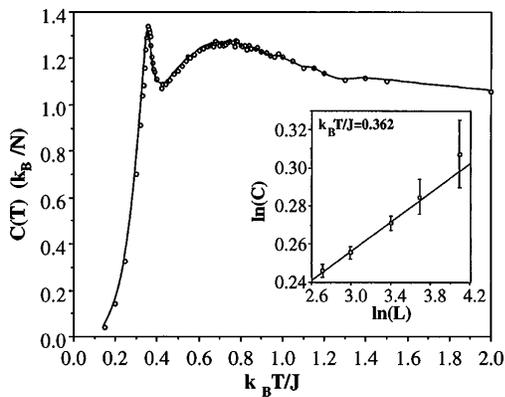

FIG. 3. Surface specific heat (in units of k_B per column) versus temperature for a $L = 30$ surface. (Inset) Finite-size scaling of $C(T)$ near preroughening $k_BT/J = 0.362$. The solid line represents a weighted least-squares fit to the data with slope $\alpha/\nu = 0.038 \pm 0.006$.

Figure 3 shows an even more pronounced peak well below roughening, near $k_BT = 0.36J$, which we attribute to PR. As shown in the inset of Fig. 3, $C(T)$ diverges weakly with L at T_{PR}, as $C(T) \sim L^{\alpha/\nu}$, with $\alpha/\nu = 0.038 \pm 0.006$. Although this peak in C signals a dramatic increase in fluctuations of the energy and the surface height, the interface width, $\sqrt{\langle\delta h^2\rangle}$, where

$$\langle\delta h^2\rangle \equiv \frac{1}{N}\sum_i \langle(h_i - \bar{h})^2\rangle \quad (4)$$

($\bar{h} = \sum_i h_i/N$ is the average surface height in a particular configuration), does not diverge with L near T_{PR} (not shown). Even well above T_{PR} (but below T_R), the interface width corresponds to fluctuations that are confined to one stacking period [6], as expected in a DOF phase. Similar behavior in $C(T)$ and $\sqrt{\langle\delta h^2\rangle}$ has been observed in a SOS model of quasiperiodic systems [10] as a series of at least two PR (termed "pseudoroughening" in Ref. [10]) transitions.

In the DOF phase columns should terminate in any of the three bilayers within a single stacking period with equal probability. Thus, we examined an order parameter

$$M \equiv \frac{3}{\sqrt{2}}[(\delta n_{AB})^2 + (\delta n_{BC})^2 + (\delta n_{AC})^2]^{1/2}, \quad (5)$$

which is normalized to 1 at $T = 0$ and tends to zero above PR (not shown). In Eq. (5), $\delta n_i \equiv n_i - \frac{1}{3}$, where n_i denotes the percentage of columns terminating in a bilayer of type i ($i = AB, BC, AC$ are the three types of bilayers in one stacking period [5,6]). We also examined the corresponding order parameter susceptibility

$$\chi_M = \frac{2N}{3k_BT}\{\langle M^2\rangle - \langle M\rangle^2\}, \quad (6)$$

which diverges at T_{PR} as $\chi_M \sim L^{\gamma/\nu}$ (Fig. 4). Based on finite-size scaling analysis of χ_M (Fig. 4, inset) and phenomenological renormalization analysis [11], we identify $k_BT_{PR}/J = 0.363 \pm 0.003$, and $\gamma/\nu = 1.24 \pm 0.01$. Assuming the scaling relations $\alpha + 2\beta + \gamma = 2$ and
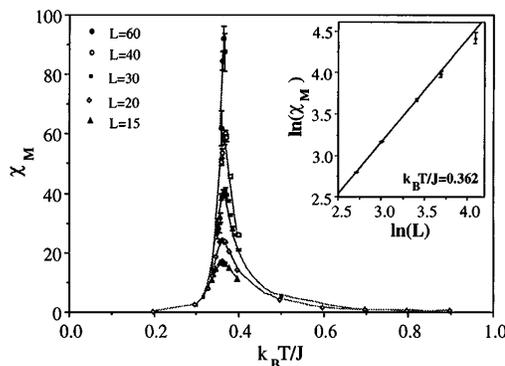

FIG. 4. Order parameter susceptibility, χ_M versus temperature for several system sizes. (Inset) Finite-size scaling of χ_M near preroughening. The solid line represents a weighted least-squares fit to the data with slope $\gamma/\nu = 1.24 \pm 0.01$.

$2 - \alpha = d\nu(d = 2)$, we thus find the exponents $\alpha = 0.038 \pm 0.006$, $\beta = 0.373 \pm 0.006$, $\gamma = 1.22 \pm 0.01$, and $\nu = 0.981 \pm 0.003$, which are significantly different from those of the 2D Ising transition and those of Ref. [4].

In the conventional theory of roughening, the step energy and step free energy vanish at T_R [12]. In systems which show PR, however, the step free energy of an isolated step vanishes already at T_{PR}, although there are still step-step interactions that stabilize the DOF phase [2,13]. Step energy densities in our DC-SOS {111} model were investigated for steps on two surfaces vicinal to {111} [6]. In both cases the steps were oriented with their edges parallel to $[1\bar{1}0]$ on average, and began as straight "triple" steps of height three bilayers (one stacking period). One set of steps was generated from misorientation of the surface toward $[11\bar{2}]$. Upon equilibration, the low-energy triple steps spontaneously separated into single bilayer-high steps (consistent with experiment [7]), and at low temperatures ($T < T_{PR}$) were found to be stable in the sense that the steps contained primarily straight segments separated by thermally generated kinks. Oppositely oriented steps were generated by misorienting the surface toward $[\bar{1}\bar{1}2]$. These steps also spontaneously separated but were found [6] to be unstable at low temperatures in that they spontaneously microfaceted into a zigzag of lower-energy segments with local edge normals along $[1\bar{2}1]$ and $[\bar{2}11]$, similar to that observed in experiments where the Si{111} surfaces were etched in weakly alkaline HF solution [14]. As $T \rightarrow T_{PR}$, the steps become isotropic and both triple-step energies approach zero (Fig. 5). Finite-size analysis of our results are consistent with a vanishing step energy for an isolated step above T_{PR}.

Because of the vanishing of the step free energy, PR is expected to have a dramatic effect on growth (and etching) of surfaces. At low T and low chemical potential driving forces $\Delta\mu$, growth (etching) takes place by two-dimensional nucleation of critical islands (pits) and their subsequent expansion and coalescence leading to layer-wise growth (etching). Under these conditions the nucleation and growth of triangular islands (pits) can be seen from our model [6]. In this regime the growth (etch) rates vary as [15]

$$R \sim \frac{\Delta\mu}{k_B T} \exp\left(\frac{-E_A}{3k_B T}\right). \qquad (7)$$

E_A is an activation barrier that depends on geometrical factors, is proportional to the square of the step free energy (η^2), and is inversely proportional to $\Delta\mu$. At sufficiently large T or $\Delta\mu$ such that E_A is of the order $k_B T$, critical island formation takes place via thermal fluctuations, growth (etch) rates become linear in $\Delta\mu$, and the surface is said to be dynamically rough [16]. The dramatic decrease in the step energy near PR facilitates dynamical roughening at lower T and $\Delta\mu$. Etch rates versus $\Delta\mu$ (Fig. 6) illustrate activated etching of surfaces in the DOF phase at sufficiently small $\Delta\mu$, and continuous etching at larger $\Delta\mu$. Assuming Eq. (7) in the activated regime, the effective step free energy (to be distinguished from the step free energy of an isolated step) is shown to be greatly affected by PR (Fig. 6, inset). Although PR significantly lowers the nucleation barrier for growth (etching), a small nucleation barrier persists in the DOF phase (i.e., $\eta^2 \neq 0$). A dramatic increase in step disordering, Si sublimation, and probable dynamical roughening has been observed by Noh *et al.*
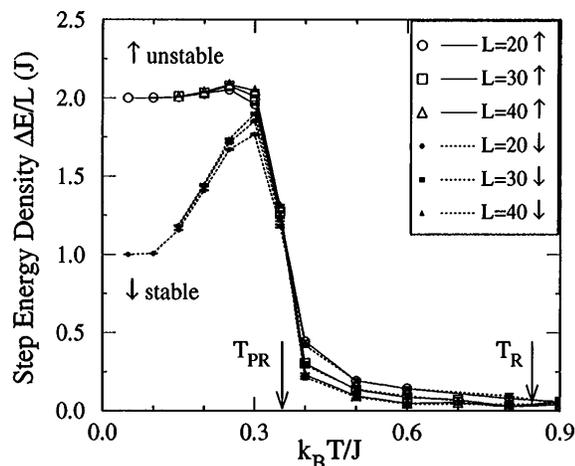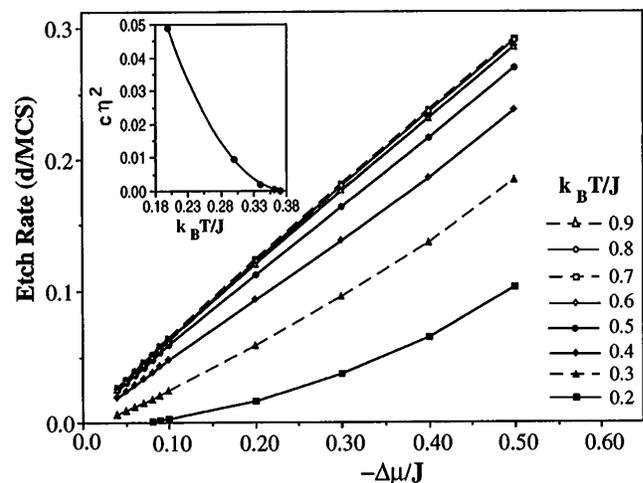

FIG. 5. Step energy densities (in units of energy J per triplet of columns projected along the average step-edge direction) for two oppositely oriented triple steps. Results are presented for surfaces of three different sizes. ↓ steps were oriented with an average edge normal along $[11\bar{2}]$, and ↑ steps were oriented with an average edge normal along $[\bar{1}\bar{1}2]$. Each point was calculated from the difference between energies of a surface with a triple step and a surface without a step. Each simulation spanned a minimum of 5×10^5 MCS.

FIG. 6. Etch rates, in units of the nearest-neighbor bond length (d) per MCS, for a $L = 63$ surface as a function of chemical potential driving force ($\Delta\mu$) for a wide range of temperatures. (Inset) Temperature dependence of $c\eta^2$ (c is a constant and η is the step free energy) for etching in the activated regime, assuming Eq. (7). Note, while small, $\eta^2 \neq 0$ at $k_B T/J = 0.36$ and 0.37.

[7] near 1275 K in experiments on vicinal Si{111} surfaces. We suggest PR as a possible explanation for their observations.

Prestipino, Santoro, and Tosatti [4] have recently investigated the PR of fcc {111} surfaces, where, as in our model, reconstruction is not a driving force for PR and there is similar degeneracy and symmetry. In contrast to our model, however, they use a RSOS model as well as further than NN interactions. When only second- and third-NN interactions are nonzero (within the RSOS model, which corresponds to infinite NN-column bond strength), they observe roughening but no PR. On the other hand, most of their results are presented for the case in which third- and fourth-NN have infinite interaction strength. In this case, they observe PR, but apparently no roughening transition. We conjecture that they may have seen distinct roughening and PR transitions had the *restricted* SOS condition been relaxed and further than NN interactions remained finite or zero. Also, in contrast to the fcc {111} results of Ref. [4], we find no evidence of diverging surface width or continuous growth strictly at T_{PR} in our DC-SOS {111} model. Nevertheless, we do find PR to significantly affect growth through the accompanying dramatic reduction in step free energy.

MC simulations of a DC (111) surface with the correct structure but without the SOS condition have been performed by van Enckevort and van der Eerden [17], and later by Tan, Ong, and Tan [18]. They determined a roughening temperature for their model at $k_B T/\phi = 0.74 \pm 0.03$, where ϕ is the solid-fluid bond formation energy. In terms of J this corresponds to $k_B T/J = 0.37 \pm 0.02$, in very good agreement with the T_{PR} of our model. We propose that the roughening temperature reported there is actually the PR temperature.

We have found that a surface model for a nontrivial crystal structure (e.g., silicon and diamond) leads to a distinct PR transition at a temperature substantially lower than that for roughening, even with very simple energetics, suggesting that PR may be more common than previously anticipated. There is good experimental evidence for PR of Si{111} near 1275 K [7]. A more detailed comparison with Ref. [7] is possible with our model, and further studies are underway.

[1] See, for example, H. van Beijeren and I. Nolden, in *Structure and Dynamics of Surfaces II: Phenomena, Models and Methods,* edited by W. Schommers and P. von Blanckenhagen (Springer-Verlag, Berlin, 1987), p. 259.

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