Thermal Roughening of a Thin Film: A New Type of Roughening Transition

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The equilibrium thermal roughening of thin Ge layers (one and two monolayers) deposited on Si(001) has been investigated with low-energy electron microscopy. A Ge-coverage-dependent roughening is observed. For two monolayers, the temperature at which imaging contrast is lost due to surface roughness is 900 ± 25 °C, between the roughening temperatures of Ge(001) and Si(001). Lower Ge coverages move this temperature closer to that of Si(001). The roughening is confined to the Ge overlayers. It is believed that this phenomenon represents a new type of surface roughening transition that should be generally applicable for heteroepitaxial films.

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Surface thermal roughening transitions, first proposed by Burton, Cabrera, and Frank [1], have been the subject of many theoretical and experimental efforts [2–4]. A surface becomes rough, i.e., undergoes a roughening transition, at the temperature at which steps form spontaneously. At this temperature, the free energy of step formation becomes zero. The step free energy is defined as $F_{\text{step}} = E_{\text{step}} - TS_{\text{step}}$ where E_{step} is the enthalpy to create a step, T is the temperature, and S_{step} is the step configurational entropy. The creation of steps is thermodynamically required at finite temperatures because it increases configurational entropy and hence reduces the surface free energy. The step density at any temperature is determined by the balance between the energy cost to create step length and the entropy gain; it increases with increasing temperature. At the transition temperature, the step density becomes unbounded.

Surface roughening is typically characterized in terms of fluctuations of the surface height induced by the creation of steps. In general, the roughening of a semi-infinite bulk material can be described by a solid-on-solid model [5–7] and the transition temperature can be estimated from the step energies. For such surfaces, at or above the roughening temperature, the height-height correlation function diverges with distance along the surface [8]. Below the roughening transition the correlation function is bounded and the surface roughness is finite.

The roughening of a thin film deposited on a substrate of a different material is much more complicated and less well understood. For physisorbed thin films, the thermodynamic properties differ in a discrete manner from layer to layer because the holding potential the substrate exerts on each layer differs in strength. Consequently, surface roughening is not observed in such films, but instead they will evaporate layer by layer with increasing temperature [9,10]. Surface roughening occurs in very thick physisorbed films, which then behave like a semi-infinite bulk.

Thermal roughening of chemisorbed films has to our knowledge not been investigated, neither experimentally nor theoretically. Yet such systems may have unique roughening behavior that is not just of academic interest. For example, in semiconductor heteroepitaxy, growth temperatures can be near or above the film roughening temperature [11]. In such situations, the roughening could greatly influence the epitaxial growth process.

Chemisorbed thin films of material B on material A may have novel roughening transitions because of the strain that builds in the film as it grows. Surface roughening in such systems could occur in two distinct ways. In one scenario, B remains on the surface of A (as a surfactant) and modifies the step energies of A. Because the projected surface area does not change, a layer of B on A simply roughens in the same fashion as pure A, modifying the roughening temperature of A [12].

In another scenario, only the deposited film B may be visualized as roughening, distinct from the underlying substrate. Because only a limited number of layers is involved, such roughening will be physically different from the conventional roughening of pure A. For example, the film surface will roughen at a different temperature from the pure-A substrate surface because the step energies of the film will be different, due to different chemical bonding and/or strain effects. In addition to the creation of steps, a roughened film will expose surfaces with different surface energies, including the substrate surface. The roughening temperature may also exhibit a dependence on film thickness, e.g., due to the thickness dependence of strain and step energy. In addition, the surface roughness of the film cannot diverge upon reaching the transition temperature because it is limited by film thickness, and thus it cannot be understood as a normal Kosterlitz-Thouless roughening transition.

In this Letter, we demonstrate the thermal surface roughening of a chemisorbed "B on A" system, Ge deposited on Si(001), by real-time monitoring of surface morphology using low-energy electron microscopy (LEEM). We demonstrate that in this heteroepitaxial system the roughening is limited to a finite number of layers, as in the second scenario presented above. The roughening temperature lies between those of pure Si(001)

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and pure Ge(001) and depends on the Ge film thickness. This dependence follows qualitatively the trend of the step energies with Ge coverage measured by scanning tunneling microscopy [13].

The experiments were carried out with a LEEM at IBM and its near twin at the University of Wisconsin–Madison [14]. A well-oriented Si(001) substrate was cleaned by repeated heating to ~1250 °C, while maintaining a pressure less than 4×10^{-9} Torr. Germanium was deposited from digermane at a pressure of 2×10^{-8} Torr and a sample temperature of 650 ± 20 °C, to coverages of one and two monolayers. The Ge coverage was determined by observing the advance of atomic-height steps during step-flow growth, and so includes an error of about 10% due to resolution limitations and possible thermal drift. All images were acquired using a $(\frac{1}{2}, 0)$ beam at ~3.5 eV electron energy.

The vanishing contrast indicates that the surface disorders. We show below that the disorder is related to the creation of atomic steps in the film. The temperature at which the contrast vanishes becomes the lower bound to the roughening temperature, at which the free energy of the rough phase becomes lower than that of the ordered phase.

We use the two-monolayer Ge film as an example. As the temperature is raised from the growth temperature to about 800 °C, domains with opposite contrast (black domains within white terraces and white domains within black terraces) appear and disappear. The domains with the opposite sign that appear within each terrace are monolayer-high 2D islands and holes formed by the creation of steps. These domains have lateral dimensions of up to 40 nm and are visible for about a second before they disappear. As the temperature continues to rise, a combination of increase in the frequency of fluctuations and a reduction in domain size (below the ~15 nm resolution of the LEEM) leads to a general reduction of contrast between terraces separated by an atomic step.

The LEED pattern was observed during a similar temperature cycle. The as-grown two-monolayer Ge-terminated surface exhibits a $(2 \times n)$ reconstruction with $n \approx 10$ [15]. The $(\times n)$ diffracted beams become indistinguishable from the background as the transition temperature is approached. Upon cooling, the $(2 \times n)$ reconstruction is recovered, with the value of n unchanged, indicating a minimal redistribution of Ge either by diffusion into the Si substrate or by desorption from the surface.

The integral and $\frac{1}{2}$-order diffracted beams have a behavior different from that of the $(2 \times n)$ beams. They remain visible through the transition, although the $\frac{1}{2}$-order intensity decreases slightly with increasing temperature while the diffuse background increases. Because the half-order beams remain throughout the transition, we can immediately rule out that the loss of contrast in the dark-field image is due to a change in the surface reconstruction.

Therefore, the loss of contrast signifies a surface roughening transition. One manifestation of thermal roughening is the formation of monolayer-high 2D islands and holes below the roughening temperature [16]. Atoms are taken out of the terrace, creating holes, and redistributed into the third (or a higher) layer, forming islands or a 2D gas of adsorbed atoms. At the transition temperature, there is sufficient structural fluctuation that on average the (2×1) and (1×2) domain populations on all terraces are the same, yielding zero contrast under our dark-field imaging conditions. The creation of many small domains is consistent with the LEED observations that the intensity of $\frac{1}{2}$-order beams is redistributed into the diffuse background and the intensity of the $(\times n)$ diffracted beams is lost as the average domain size becomes too small (on the order of a few n units, ~2–3 nm), so that little long-range order exists.

Although substantial rearrangement of atoms occurs, this rearrangement is limited to the outer layers. Evidence of significant rearrangement comes from the emergence of reconstructed-domain boundaries upon cooling, as seen clearly in Fig. 2. These domain boundaries, arising from the nucleation of translational antiphase reconstruction domains, represent an intermediate length scale (~100 nm) that appears in the images as snakelike loops caused by the boundaries themselves or by small islands that form preferentially at the boundaries [17]. These loops disappear above the transition temperature and reappear in different locations below the transition temperature as new antiphase domains nucleate in uncorrelated positions from cycle to cycle.

Substrate steps, on the other hand, provide the key evidence that the roughening is limited to a finite number of layers with a finite roughness, rather than the conventional roughening of a semi-infinite bulk. In Fig. 1(c), the large-scale undulations of the atomic steps, caused by the sample misorientation and therefore a part of the substrate morphology, are largely unchanged from the starting surface [see Fig. 1(a)]. If the sample had undergone a bulk 3D roughening transition, the surface roughness would diverge logarithmically. Upon cooling, the surface would smoothen, recovering the same average step density, but the local step structure would not survive the transition. On the other hand, if only the film roughens, the steps, which are replicated in the film, will remain essentially unchanged as the temperature is raised or lowered, although they may wander about their initial positions as the film disorders. Figure 2 demonstrates that after many cycles the overall terrace structure remains intact. The signature of unvarying local substrate step density is decisive in establishing that only the adsorbed film disorders.

The roughening temperature can be determined from the condition of zero contrast. We have determined quantitatively the contrast at a given temperature by digitizing representative experimental images and analyzing the average line profile across a step,

$$\text{Contrast} = \frac{I_{\text{bright}} - I_{\text{dark}}}{I_{\text{bright}} + I_{\text{dark}}}, \tag{1}$$

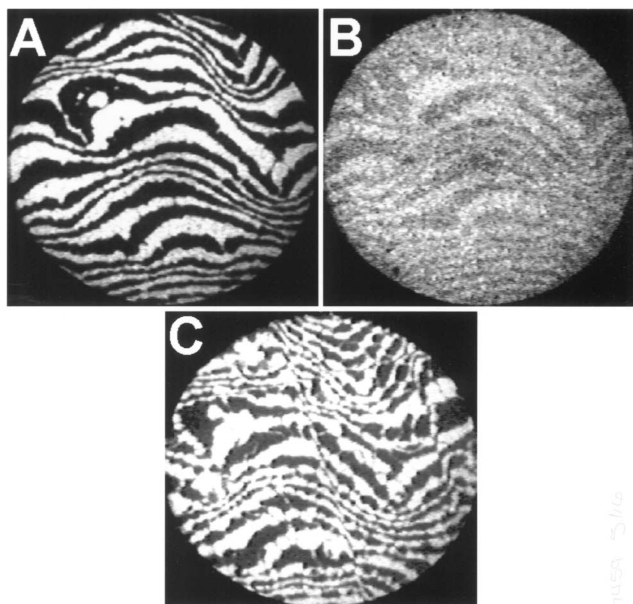

FIG. 1. (a) Dark-field LEEM image of Si(001) taken at 650 °C for a coverage of 2 monolayer (ML) of Ge, showing black and white intensity variations for adjacent terraces separated by an atomic step. The small islands on the terraces are the start of the third ML. The sample temperature was ramped at about 2 °C/sec to approximately 850 °C, then increased to ~10 °C/sec to reach the temperature at which the contrast vanishes. (b) LEEM image of the 2-ML Ge-covered surface at approximately 860 °C. The contrast has nearly disappeared at this temperature, although the signature from the substrate steps is still visible. (c) An image of the surface after quenching from high temperature to 650 °C. The "snakelike" features within and crossing the terraces are locations of antiphase domain boundaries. See also Fig. 2. Field of view is 4 μm.

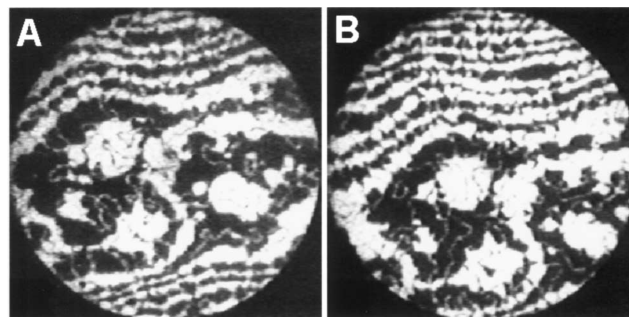

FIG. 2. The 2-ML Ge-covered surface after quenching to 650 °C from the roughening temperature after (a) two cycles, (b) five cycles. Note that the domain boundary locations change position after every cycle, but the overall terrace structure dictated by the underlying substrate is maintained, indicating that the substrate does not roughen. These images are taken from a different sample location than in Fig. 1. Thermal drift has shifted the image slightly downwards from (a) to (b). Field of view is 4 μm.

where $I_{\rm bright}$ is the average intensity of the initially bright (e.g., 2×1) terraces and $I_{\rm dark}$ is the corresponding intensity of the initially dark (e.g., 1×2) terraces at any given time.

Figure 3 shows the measured contrast variation with increasing temperature. For the two-monolayer Ge film on Si(001), the contrast vanishes at the roughening temperature of 900 ± 25 °C. For the one-monolayer film, the exact roughening temperature is not known because we did not raise the sample temperature above 900 °C to avoid possible removal of Ge from the surface. Nevertheless, we can deduce from Fig. 3 that the roughening temperature of a one-monolayer film (~1000 °C) would be higher than that of a two-monolayer film, indicating an increase of the roughening temperature with decreasing film thickness.

The thermodynamics underlying the roughening of a finite film is much more complicated than that of the conventional roughening of a semi-infinite bulk. For a monocomponent semi-infinite system, the roughening is solely defined by the "surface" step free energies, allowing the roughening temperature to be calculated accurately using a solid-on-solid model [5–7]. For example, using the measured step energies of clean Si(001) [6,18] and Ge(001) [7], the model predicts the roughening temperature of Si(001) and Ge(001) to be about 1230 °C and 630 °C, respectively, in good agreement with experimental values of about 1200 °C [6] and 680 °C [19]. For a thin heteroepitaxial film, at least two additional contributions exist. One, the roughening will expose layers having different surface energies, including the substrate surface. Two, steps at different levels may have different energies, due to a buildup of strain. These complications make a calculation of roughening temperatures via the solid-on-solid model less reliable. We estimate the roughening temperature using the one known energetic component, the measured effective step energies for ~one- and ~two-monolayer Ge films on Si(001) [13]. We calculate a roughening temperature of 730 ± 50 °C for a two-monolayer film, about 15% below the experimental value. For the

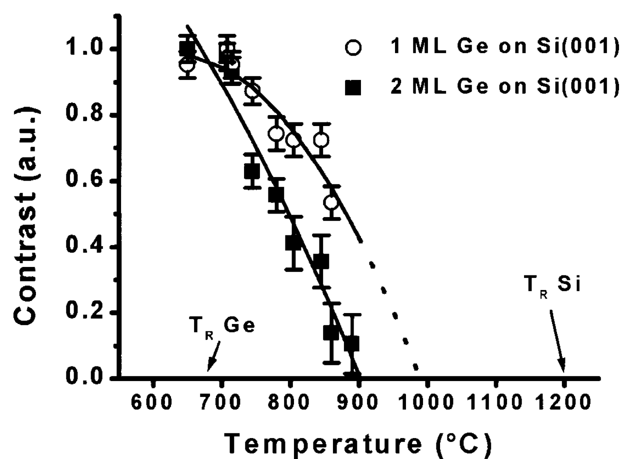

FIG. 3. LEEM image contrast as a function of temperature. Squares: 2 ML Ge; circles: 1 ML Ge. As the Ge coverage decreases, the roughening temperature increases. The roughening temperature for 2-ML Ge is 900 ± 25 °C; the projected value for 1 ML is 1000 ± 100 °C. The curves are to guide the eye.

single-monolayer film, the calculation yields a roughening temperature of 1010 ± 100 °C, close to the extrapolated experimental value. This result is entirely reasonable. First, the decrease of the roughening temperature with increasing film thickness agrees with experiment, indicating that step energies account for a major part of the energy cost for roughening. Second, it is likely that the measured effective step energies for the one-monolayer film represent a better approximation to the total energy needed for roughening than for a two-monolayer film. For the two-monolayer film, the step energies are likely a smaller fraction of the total energy for roughening—the effective step energies themselves suggest a lower roughening temperature than is actually the case. So, for example, the higher step energies of the first monolayer of Ge (which are not reflected in the effective step energies of the second monolayer) played a role in the roughening.

In conclusion, we have utilized the high-temperature *in situ* growth and imaging capabilities of low-energy electron microscopy to investigate the roughening of a thin heteroepitaxial film, Ge on Si(001). We show that the thermal roughening is confined to the heteroepitaxial layers, making this roughening transition fundamentally different from conventional surface roughening. We expect this result to be general for all B-on-A heteroepitaxial films of limited thickness. The roughening temperature of a two-monolayer Ge film on Si(001) is 900 ± 25 °C, lying between those of pure Ge(001) and pure Si(001). The roughening temperature depends on film thickness. Our calculations confirm the dependence of transition temperature on film thickness. A conventional solid-on-solid model cannot adequately include all the contributions to describe the roughening quantitatively. We hope that our results will stimulate the development of more comprehensive models of heteroepitaxial film roughening.

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