Critical Epinucleation on Reconstructured Surfaces and First-Principle Calculation of Homonucleation on Si(100)

Raj Ganesh S. Pala and Feng Liu

Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

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We introduce the concept of "critical epinucleation" to distinguish nucleation on surfaces with and without reconstruction. On a reconstructed surface, the critical classical nucleus is stable against dissociation, but may not yet break the underlying surface reconstruction. Consequently, there must exist a "critical epinucleus" that is not only stable but also has established the epiconfiguration by unreconstructing the underlying substrate. We illustrate this concept by first-principle calculation of homonucleation on reconstructed Si(001) surface where the critical epinucleus consists of six adatoms.

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A crucial event in the early stages of growth is nucleation of two-dimensional (2D) islands from diffusing adatoms on the surface [1–4]. The classical mean-field nucleation theory establishes a useful scaling relationship for the density of stable nuclei as a function of adatom's deposition rate and surface diffusion coefficient [1–5]. The dynamics of island nucleation process manifests the underlying adatom interactions [1–7]. However, fundamental understanding of nucleation process is still incomplete and attempts are being made to incorporate important effects like surface defects [8], reactions [9], long-range surface mediated interactions [10–15], and lack of a stable critical nucleus [16]. Here, we introduce a new concept of "*critical epinucleation*," which will be most relevant in epitaxial growth on a *reconstructed* surface.

The critical classical nucleus (CCN) is defined as the smallest island whose probability of growth is greater than decay. This definition assumes implicitly that the nucleus has established the correct epitaxial configuration forming bulklike bonding with the substrate needed for further growth. This is generally true for growth on surfaces without reconstruction, but may often be invalid on reconstructed surfaces. Surfaces, especially semiconductor surfaces, reconstruct by forming new surface bonds, such as the surface dimers on Si(001) [2]. These reconstructed surface bonds have to be broken for epitaxial growth to proceed, which entails an energy penalty. Hence, the CCN, although stable against dissociation, may not have the correct epiconfiguration because the underlying substrate may not yet have "bulklike" bonding. Therefore, there must exist an additional structural entity, distinct from the CCN, which is not only stable but also establishes the correct epiconfiguration by unreconstructing the substrate. We define the smallest of such structural entity as the "critical epinucleus" (CEN).

The formation of CCN arises from the competition between two energetic factors: energy penalty due to island step edge and energy gain due to bond formation in the "bulk" of the island. For a complete description of nucleation on a reconstructed surface, an additional term—the energy needed for breaking the reconstructed surface bonds—must be taken into account, leading to the introduction of CEN. In general, the CEN is larger than the CCN because of this additional energy term; their size difference will be most apparent at low temperatures when the critical nucleus is small [7].

To confirm the existence of CEN, we have performed first-principle calculations of homonucleation on Si(001) surface as a model system. We find that CCN is comprised of a single addimer [17] in a nonepiconfiguration. The most stable 2D island comprised of two addimers is also in nonepiconfiguration. But a *metastable* two-addimer island with the correct epiconfiguration does exist. With three addimers, the most stable island is found to have the correct epiconfiguration with the underlying substrate unreconstructed to bulklike bonding, and all the other non-epi-three-addimer islands have higher energy. Thus, for Si(001) homoepitaxy, the CEN consists of six adatoms (three addimers) whereas the CCN consists of two adatoms [17]. Furthermore, we analyze the formation and stability of CCN versus CEN using general chemical bonding arguments and discuss the implications of critical epinucleation.

We model the Si(001) surface using plane wave pseudopotential total energy method as elaborated in previous calculations [18–20]. The supercell consists of a six-layer slab with the bottom Si layer saturated by H. To identify the CEN, we place a 2D island on the surface and determine its optimal structure and stability as a function of increasing size from 2 to 4 to 6 adatoms, and the surface cell is scaled, respectively, up to (4×4), (6×6), and (8×8) to ensure the convergence. For each island, we consider both the epi and nonepiconfiguration to find out when the epi-island becomes energetically favorable.

We first discuss the smallest 2D island comprised of an addimer. It is considered the CCN for growth on Si(001) [2,3,17]. In Fig. 1, we denote the addimer in two different configurations on top of dimer rows as $D1$ and $D2$, and in

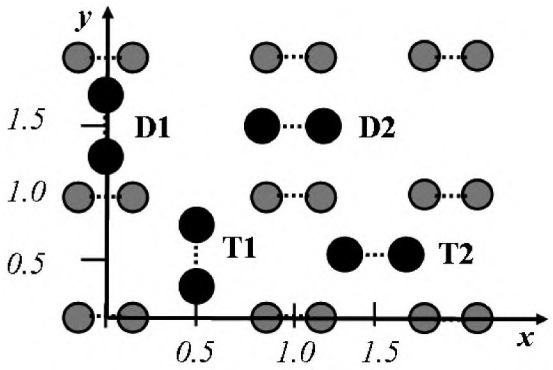

FIG. 1. A schematic top view of Si(001)-(2×1) surface dimers (gray dots) and four addimer configurations (black) denoted as $D1$, $D2$, $T1$, and $T2$. The addimer positions are specified by the surface Cartesian coordinates.

the trough as $T1$ and $T2$. Note that $D1$ and $T1$ have the correct epiorientations, perpendicular to the surface dimers as required by the tetrahedral bonding of Si [2], while $D2$ and $T2$ have the nonepiorientation. Our calculations show that all four addimer configurations do not lead to epibonding of the substrate; i.e., the substrate beneath them remains dimerized. $D2$ is found to be the most stable addimer, in agreement with previous studies [18]. It has neither an epiorientation nor an epibonding. Thus, it is clear the CCN is a non-epi-island.

Next, we consider islands with a pair of addimers, in a variety of structures that can be obtained by different combinations of two single addimers. Amongst the many tested, some low-energy island configurations are listed in Table I. They are denoted by individual addimer configurations and their relative positions specified by the surface coordinates defined in Fig. 1. The most stable configuration is $\{D2(0.0, 0.5), D2(0.0, 2.5)\}$ with two $D2$ addimers on the same dimer row separated by a spacing of two units along the y axis [Fig. 2(a)]. Clearly, it is a non-epi-island with neither epiorientation nor epibonding. Its high stability stems from the high stability of individual $D2$ addimer. In fact, most low-energy islands contain one or two $D2$ addimers as shown in Table I. However, in contrast to the single-addimer island, a two-addimer island may adopt an epiorientation to break the surface dimers in the $\{D1(0.0, 0.5), T1(0.5, 0.5)\}$ configuration, as shown in Fig. 2(b), where the broken surface dimer bonds are indicated by broken lines. But its energy is ~0.21 eV higher than that of the most stable island as listed in Table I. Thus, this two-addimer epi-island is metastable. It does not yet constitute the "critical" epinucleus because it is unstable against dissociation/rearrangement to other more stable 2D islands of the same size.

The energies (same notations as in Fig. 1) of some low-energy 2D islands with three addimers are listed in Table II. We observe that the most stable island has the configuration $\{T1(0.0, 0.5), D1(0.5, 0.5), T1(1.0, 0.5)\}$, as shown in Fig. 3. This island not only has all the three addimers in epiorientation but also induces correct epibonding to the underlying substrate by breaking the sub-

TABLE I. Relative energies of island configurations with two addimers. The epi-island configuration is in bold font.

Island Configuration	Energy (eV)
$\{D2(0.0, 0.5), D2(0.0, 2.5)\}$	−0.21
$\{D2(0.0, 0.5), D1(0.0, 2.5)\}$	−0.15
$\{D2(0.0, 0.5), D2(1.0, 2.5)\}$	−0.13
$\{T2(0.5, 0.5), T2(1.5, 2.5)\}$	−0.12
$\{D2(0.0, 0.5), D2(1.0, 0.5)\}$	−0.1
$\{D2(0.0, 0.5), D2(1.0, 2.5)\}$	−0.07
{D1(0.0, 0.5), T1(0.5, 0.00}	0.0

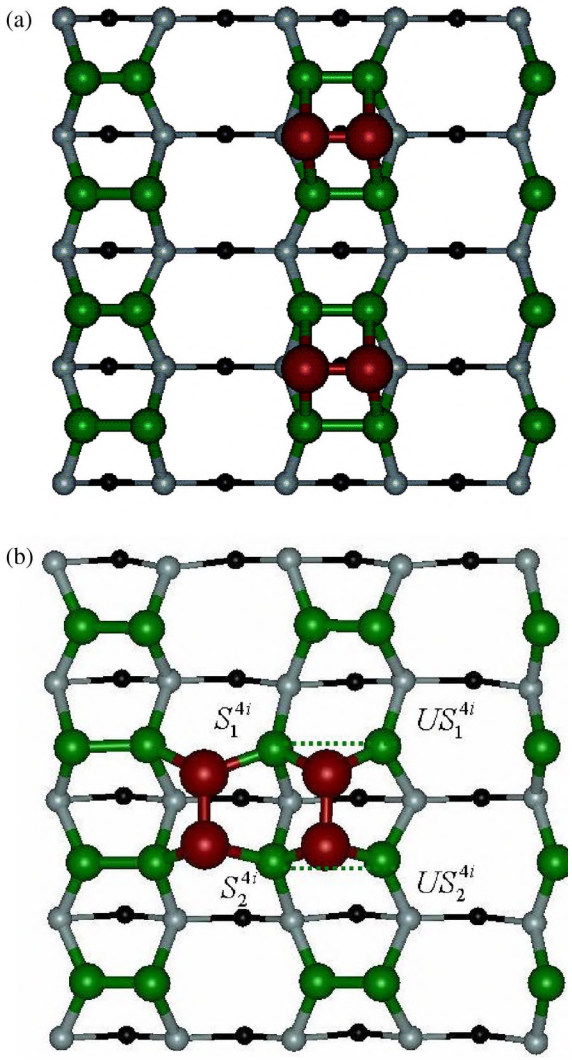

FIG. 2 (color online). Structure of the most stable non-epi- (a) and metastable epi-island (b) consisting of two addimers (red). The atomic size scales with its height, with the surface atoms largest.

TABLE II. Relative energies of island configurations with three addimers. The epi-island configuration is in bold font.

Island Configuration	Energy (eV)
{T1(0.0, 0.5), D1(0.5, 0.5), T1(1.0, 0.5)}	0.0
{*D*2(0.0, 0.5), *D*2(0.0, 1.5), *D*2(0.0, 2.5)}	0.24
{*T*1(0.5, 0.5), *D*1(1.0, 0.5), *T*2(1.5, 0.5)}	0.35
{*D*2(0.0, 0.5), *D*2(0.0, 2.5.0), *D*2(0.0.4.5)}	0.39
{*T*1(0.5, 0.5), *D*2(1.0, 0.5)*T*2(1.5, 0.5)}	0.62
{D1(0.0, 0.5), T1(0.5, 0.5), D1(1.0, 0.5)}	1.07
{*D*1(0.0, 0.5), *T*2(0.5, 0.5)*D*1(1.0, 0.5)}	1.29

strate dimer bonds between atoms S_1^{6i} and S_2^{6i}, and between S_3^{6i} and S_4^{6i} in Fig. 3. All other island configurations, including the one consisting of three $D2$ addimers, {$D2$(0.0, 0.5), $D2$(0.0, 0.5), $D2$(0.0, 0.5)}, have higher energies as shown in Table II. Thus, we identify the three-addimers island in the configuration {$T1$(0.0, 0.5), $D1$(0.5, 0.5), $T1$(1.0, 0.5)} to be the critical epinucleus for homoepitaxy on Si(001).

The above calculations indicate that a single-addimer epi-island does not exist, a two-addimer epi-island is metastable, and a three-addimer epi-island constitutes the CEN. We may qualitatively rationalize such a stability trend based on atomic valency and the analysis of chemical bonding. The number of bonding neighbors decides an atom's hybridization state and optimal bond lengths and bond angles, and hence influences the relative stability of islands of different size.

As Si is a tetra-valent element, when a single addimer binds to the Si(001) surface in the epiorientation ($D1$ in Fig. 1), all four surface Si atoms beneath the addimer are saturated only if the surface dimer bond remains intact. On the other hand, if the surface were to unreconstruct by breaking surface dimer bonds, these four surface atoms' saturation would be lost. Consequently, a single addimer, even in the epiorientation, does not induce epibonding with

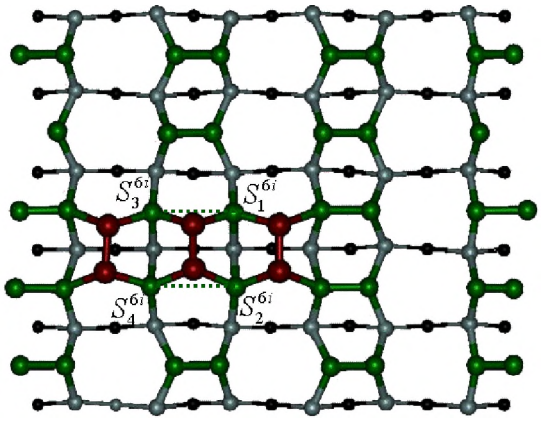

FIG. 3 (color online). Structure of the critical epinucleus for Si(001) homoepitaxy consisting of three addimers. Same notations as in Fig. 2.

the substrate. For an epioriented two-addimer island, as shown in Fig. 2(b), bonding of the two addimers to the two surface Si atoms [denoted by S_1^{4i} and S_2^{4i} in Fig. 2(b)] saturates the valency of these two surface atoms after breaking the reconstructed surface dimer bonds. But the two atoms at the island edge [indicated by US_1^{4i} and US_2^{4i} in Fig. 2(b)] are under coordinated with only three neighbors. Thus, for an epi-island comprised of two addimers, the ratio of substrate atoms with saturated valency over those with unsaturated valency is 66%. For the three-addimer CEN, all the surface atoms after breaking the surface dimer bonds are saturated, as shown in Fig. 3. Thus, the valency saturation of the surface atoms can be used as an effective measure for determining the stability of epi-island as surface dimers are broken. This is also reflected by comparing another three-addimer epi-island {$D1$(0.0, 0.5), $T1$(0.5, 0.5), $D1$(1.0, 0.5)} with CEN. This $D1$-$T1$-$D1$ island is metastable with an energy ~1 eV higher than CEN, as shown in Table II, because the valency of four surface atoms at the edge of this island is not saturated, while those in the stable $T1$-$D1$-$T1$ CEN are all saturated. In other words, the $D1$-$T1$-$D1$ island, terminated by two nonrebonded S_B step edges, has a higher energy than the CEN, terminated by two rebonded S_B step edges [21].

It has been shown that [22] the CCN, the $D2$ addimer is formed by a simple rotation from the metastable $D1$ addimer, which is in turn formed by collision of two adatoms diffusing on top of the dimer rows. Hence, the dynamics of CCN formation depends on the energetics of adatom's surface diffusion, binding, and addimer rotation. On the other hand, the CEN, a three-addimer island, is unlikely to form via the most stable two-addimer island {$D2$(0.0, 0.5), $D2$(0.0, 2.5)} in Fig. 2(a), but instead via the metastable two-addimer island {$D1$(0.0, 0.5), $T1$(0.5, 0.5)} in Fig. 2(b) by adding another addimer in the trough next to it. (Adding another addimer on top of the dimer row would result in a metastable {$D1$(0.0, 0.5), $T1$(0.5, 0.5), $D1$(1.0, 0.5)} island as discussed above.) The intermediate metastable {$D1$(0.0, 0.5), $T1$(0.5, 0.5)} island may also dissociate into the more stable two-addimer island, {$D2$(0.0, 0.5), $D2$(0.0, 2.5)}, which would slow down the dynamics of critical epinucleation and the formation rate of CEN.

The existence of CEN has important implications on the dynamics of nucleation and evolution of island growth due to changes in the energy landscape. In general, we may expect that the nucleation energy as a function of cluster size adopt a shape as shown in Fig. 4. In contrast to classical nucleation (dashed line in Fig. 4), the epinucleation proceeds (solid line) via three stages: first, formation of CCN, characterized by an energy maximum (point C); second, a transition region in which the non-epi-island transforms to epi-island; finally, formation of CEN, characterized by another energy maximum (point E). The transition region may have a local minimum due to the existence of metastable epi-island [point M, e.g., the meta-

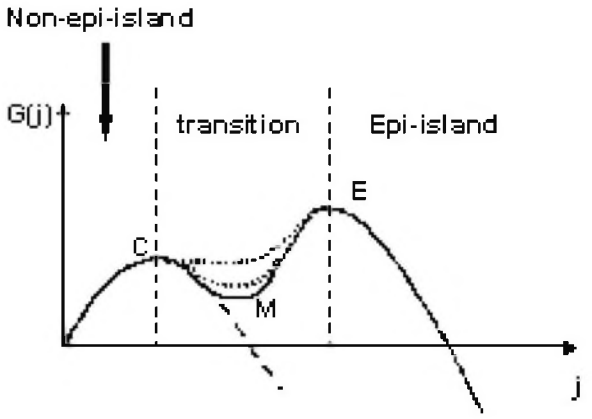

FIG. 4. Schematic illustration of energy landscape of critical epinucleation, showing nucleation energy as a function of island size.

stable two-adddimer island on Si(001)] or just a shoulder depending on the system and growth condition. However, the three regions will generally exist and so the formation rate of E is always different from C as the energy landscape involved is different.

Based on the modified nucleation energy landscape, as shown in Fig. 4, one may revise the classical nucleation theory. If we retain the classical nucleation theory using CCN, we must introduce a new regime to describe the growth from CCN (point C) to CEN (point E). The energetics and the dynamics of this regime must be different from further growth of CEN to larger epi-islands. On the other hand, if we take CEN as the "true" nucleus for epitaxial growth, we need to modify the energetics and dynamics of nucleation as was done for incorporating other effects [6,11–13], because in this case one convolutes the two physically distinct processes, classical nucleation and epinucleation, into a single process.

Specifically, for Si(001) nucleation, our calculations show that C point is monomer, transition region contains 2- to 4-atom island where non-epi- and epi-islands varying their relative stability, and E point is a pentamer. The distinction between CCN and CEN will be more pronounced at low temperature, because at high temperature, critical nucleus is a very large epi-island containing hundreds of dimers [7]. Its growth dynamics is likely dominated by the addition of four adatoms (two addimers) at a time to maintain the stable rebonded S_B step edges [23]. Thus, the concept of CEN is more valid at low temperature where the adatoms are the predominant diffusing species [24].

In conclusion, we propose a new concept of "critical epinucleation," which is especially relevant for a more complete description of nucleation and epitaxial growth on reconstructed surfaces. We illustrate the proposed concept by demonstrating its existence in the context of Si(001) homoepitaxy. First-principles calculations show that the CEN consists of three addimers in contrast to the CCN consisting of a single addimer. Furthermore, we give a qualitative analysis to compare the relative stability of epi-island of various sizes in terms of surface Si atom's valency saturation. We believe the concept of "critical epinucleation" should also be generally extendable to epitaxy on surfaces that are not reconstructed, but wherein the growing 2D island adopts a structure different from the underlying bulk substrate to optimize local chemical bonding within the growing island.

[1] J. A. Venables, Philos. Mag. **27**, 697 (1973).
[2] F. Liu and M. G. Lagally, in *The Chemical Physics of Solid Surfaces*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1997), Vol. 8, p. 258.
[3] Z. Zhang and M. G. Lagally, Science **276**, 377 (1997).
[4] A. Pimpinelli and J. Villain, *Physics of Crystal Growth* (Cambridge University Press, Cambridge, England, 1998).
[5] Y. W. Mo *et al.*, Phys. Rev. Lett. **66**, 1998 (1991).
[6] J. A. Venables and H. Brune, Phys. Rev. B **66**, 195404 (2002).
[7] W. Theis and R. M. Tromp, Phys. Rev. Lett. **76**, 2770 (1996).
[8] G. Haas *et al.*, Phys. Rev. B **61**, 11105 (2000).
[9] P. Kratzer and M. Scheffler, Phys. Rev. Lett. **88**, 036102 (2002).
[10] B. Fischer *et al.*, Phys. Rev. Lett. **82**, 1732 (1999).
[11] K. A. Fichthorn and M. Scheffler, Phys. Rev. Lett. **84**, 5371 (2000).
[12] S. Ovesson, Phys. Rev. Lett. **88**, 116102 (2002).
[13] S. Ovesson *et al.*, Phys. Rev. B **64**, 125423 (2001).
[14] A. Bogicevic *et al.*, Phys. Rev. Lett. **85**, 1910 (2000).
[15] J. Repp *et al.*, Phys. Rev. Lett. **85**, 2981 (2000).
[16] C. Ratsch *et al.*, Surf. Sci. **329**, L599 (1995).
[17] To be consistent with the introduced concept of critical epinucleation, we adopt this slightly modified definition of CCN. CCN is defined in classical nucleation theory as the smallest nucleus that becomes more stable with the addition of one more atom.
[18] G. Brocks and P. J. Kelly, Phys. Rev. Lett. **76**, 2362 (1996).
[19] F. Liu and M. G. Lagally, Phys. Rev. Lett. **76**, 3156 (1996).
[20] R. G. S. Pala and F. Liu, J. Chem. Phys. **120**, 7720 (2004).
[21] F. Liu, C. T. Salling, and M. G. Lagally, Surf. Sci. **370**, L213 (1997).
[22] Z. Zhang *et al.*, Phys. Rev. Lett. **74**, 3644 (1995).
[23] N. Kitamura *et al.*, Phys. Rev. B **48**, 5704 (1993).
[24] At high temperature, the diffusion species might involve dimers and clusters in addition to adatoms, but these are irrelevant to our model because there is no distinction between CCN and CEN at high temperature.