10-2010

Stochastic coarsening model for Pb islands on a Si(111) surface

G. P. Zhang
Renmin University of China

Myron Hupalo
Ames Laboratory, hupalo@ameslab.gov

M. Li
Renmin University of China

C. Z. Wang
Ames Laboratory, Iowa State University

James W. Evans
Iowa State University, evans@ameslab.gov

See next page for additional authors

Stochastic coarsening model for Pb islands on a Si(111) surface

Abstract

The coarsening behavior of individual Pb islands on Si(111) surface has been studied by scanning tunneling microscopy. Traditionally island decay follows a smooth power-law dependence on the time until disappearance. In Pb/Si(111), some unstable islands are inactive for a long time but once their decay is triggered they suffer a "sudden death." Four-layer islands are found to decay rapidly, increasing the area covered by seven-layer islands. All islands, decaying or otherwise, are accompanied by island size fluctuation which involve a large number of perimeter atoms moving collectively as a "quantized" unit. A stochastic model is developed to elucidate the mechanism behind this coarsening behavior of Pb islands. The distinct evolution of the islands with different heights is correctly predicted, and the size fluctuations of islands and the sudden death behavior observed in island coarsening are also recovered. The key ingredients are incorporation of accurate non-Gaussian statistics of the size fluctuations and also accounting for size changes in large quantized bursts.

Disciplines

Astrophysics and Astronomy | Physics

Comments

This article is from *Physical Review B* 82 (2010): 165414, doi:10.1103/PhysRevB.82.165414. Posted with permission.

Authors

G. P. Zhang, Myron Hupalo, M. Li, C. Z. Wang, James W. Evans, Michael C. Tringides, and K. M. Ho

Stochastic coarsening model for Pb islands on a Si(111) surface

G. P. Zhang,[1,2] M. Hupalo,[1] M. Li,[2,1] C. Z. Wang,[1] J. W. Evans,[1] M. C. Tringides,[1] and K. M. Ho[1]
[1]*Ames Laboratory-US DOE, Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[2]*Department of Physics, Renmin University of China, Beijing 100872, People's Republic of China*
(Received 12 March 2010; revised manuscript received 9 August 2010; published 7 October 2010)

The coarsening behavior of individual Pb islands on Si(111) surface has been studied by scanning tunneling microscopy. Traditionally island decay follows a smooth power-law dependence on the time until disappearance. In Pb/Si(111), some unstable islands are inactive for a long time but once their decay is triggered they suffer a "sudden death." Four-layer islands are found to decay rapidly, increasing the area covered by seven-layer islands. All islands, decaying or otherwise, are accompanied by island size fluctuation which involve a large number of perimeter atoms moving collectively as a "quantized" unit. A stochastic model is developed to elucidate the mechanism behind this coarsening behavior of Pb islands. The distinct evolution of the islands with different heights is correctly predicted, and the size fluctuations of islands and the sudden death behavior observed in island coarsening are also recovered. The key ingredients are incorporation of accurate non-Gaussian statistics of the size fluctuations and also accounting for size changes in large quantized bursts.

DOI: 10.1103/PhysRevB.82.165414 PACS number(s): 68.43.Jk, 68.35.Fx, 68.37.Nq, 68.65.Fg

Growth and coarsening on surfaces have been the focus of intensive studies in the past few decades.[1–3] In traditional epitaxial systems, the coarsening of two-dimensional or three-dimensional islands formed during growth is expected to be dominated by Oswald ripening (OR), where diffusion of material across terraces is driven by differences between chemical potentials of islands with varying sizes. Smaller islands with higher chemical potentials shrink while larger islands with lower chemical potentials grow in size via the transport of adatoms from smaller to larger islands.[1,2] Although it works well for many-surface deposition systems, this classical OR theory was challenged by recently discovered coarsening phenomena in Pb islands on Si(111) surface.[4] A fast coarsening behavior of Pb islands was observed and attributed to quantum-size effects impacting the stability of islands with different heights and fast mass transport in the dense wetting layer.[4–7] In addition, according to classic OR theory, the decay in area of unstable islands obeys simple power law in the time until disappearance. The exponent depends on whether the decay is diffusion-limited or interface-limited (the latter case being associated with the presence of a substantial additional barrier inhibiting attachment of adatoms to islands). Another aspect of nonclassical behavior in Pb/Si(111) is revealed in the novel way in which unstable islands decay: the islands can remain unchanged for a very long time but when their decay is initiated it is catastrophic. We use the term "sudden death" to describe this very unusual and nonclassical behavior. It is the goal of the current paper to explain this intriguing phenomenon. Its broader implication is that this is another reason why the formation of stable height islands in Pb/Si is unusually fast.

In this paper, we have performed a detailed analysis of coarsening dynamics of Pb islands on Si(111) surface using scanning tunneling microscopy (STM), revealing the presence of strong fluctuation in the sizes (areas) of individual Pb islands surface during the coarsening process. This behavior occurs regardless of the height of the islands. Moreover, we also found that once the decay of an island is triggered, the island will disappear in a very short time. This sudden death behavior is observed for islands with both stable and unstable heights. This novel coarsening dynamics is intriguing and cannot be explained by either the classical coarsening theory or our previous mean-field theory of quantum-size-effect-mediated coarsening.[5,6]

In order to understand the mechanism of the area fluctuation and sudden death of Pb islands during the coarsening process, we develop a stochastic coarsening model for this interesting system. In this model, the fluctuation of island sizes are incorporated into a stochastic prescription of growth or decay of individual islands which are coupled through the wetting layer. Large quantized fluctuations are observed that involve hundreds of atoms that move collectively and the unusual mobility of the wetting layer facilitates their formation and fluctuating motion. The stochastic prescription leads to sudden decay of islands. As we will show later, the time evolution of islands with various heights from our theoretical model is in good agreement with experimental observations.

In our previous STM experiments,[6] the average coarsening behavior of Pb islands with different heights was investigated. It was found that the average area of four-layer islands decreases quickly, but the average area of seven-layer islands increases. As noted previously the initial distribution consists mainly of four- and seven-layer islands and a very small number of five- and six-layer islands. Over the duration 100 min at 205 K of these experiments, most of the four-layer islands decay and the area covered by the seven-layer islands correspondingly increases. This was accounted for by the strong dependence of the chemical potential on island height. Turning to stochastic aspects of the system, in fact we observed fluctuations the areas of islands of all heights. The small number of five-layer and six-layer islands remains unchanged despite these fluctuations so their average areas do not change much.

In our current STM experiments, we focused on the coarsening of individual Pb islands on Si(111) surface. The experimental details are introduced in Refs. 4–6, the temperature during coarsening is $T=205$ K, and the coverage is $\theta=1.4$ ML. Figure 1 shows the time evolution of areas of individual islands with different heights. It is clear that the coarsening behavior of islands with different heights is quite

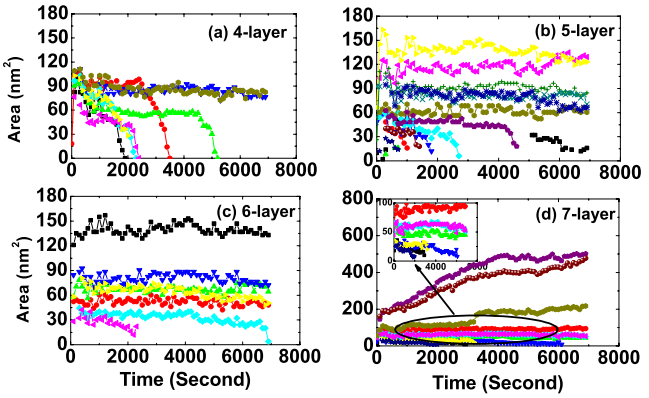

FIG. 1. (Color online) The experimentally measured area evolution of (a) four-layer, (b) five-layer, (c) six-layer, and (d) seven-layer islands vs time at $T=205$ K and $\theta=1.4$ ML. The few five- and six-layer islands do not change either because they are laterally big or because their environment does not have seven-layer superstable islands.

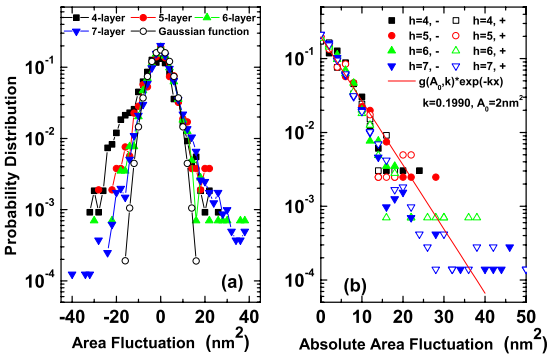

FIG. 2. (Color online) The probability distribution of area fluctuation of Pb islands extracted from the experiment in the time interval of 100 s used for the acquisition of large 500×500 nm^2 areas. Statistical data from (a) all islands and (b) islands with no obvious growth or decay. In (b) "–" and "+" stand for negative and positive area fluctuation, respectively.

different. For four-layer islands, although the initial areas of all four-layer islands are almost the same as shown in Fig. 1(a), the coarsening behavior of four-layer islands is uncorrelated with their initial sizes. While the areas of some islands do not change much during observation time, some islands disappear quickly, and some others shrink gradually at first, and then suddenly disappear. For five-layer islands, the sudden death during coarsening is also observed. However, the islands with bigger areas are more stable. For six-layer islands, almost all do not change much in size, but fluctuate around their initial areas. This is a result of their lower chemical potential with respect to four-layer islands, and on the other hand since there are only a few of them their persistence might be related to their large lateral size and being surrounded by stable seven layer so there is no mass available to "feed" them to grow. For seven-layer islands, however, some islands keep their initial island sizes, but others become bigger during coarsening. The phenomena of sudden death of Pb islands are also observed in six- and seven-layer islands although infrequently. Around 15–20 out of 158 seven-layer islands, i.e., about 10%, decay and they have initial areas from 10 to 30 nm^2.

The area fluctuation and sudden death behavior observed in the coarsening of individual Pb islands on Si(111) surface are totally different from the coarsening behavior observed in traditional epitaxial systems. It has been shown that mass transport via the dense wetting layer is much faster and more efficient than usual surface diffusion processes.[5,8–12] Islands communicate via the wetting layer with unstable islands "feeding" the wetting layer while stable islands being "fed" by the wetting layer even when they are located far away from the decaying unstable islands since the wetting layer moves collectively in liquidlike fashion. Thus, "anomalous" fluctuations might be expected at the edge of the islands because there is no need to wait for material accumulate and build the large "burstlike" fluctuations since it is easily transported from neighboring islands through the wetting layer. Moreover, single fluctuation of individual islands can include processes such as the entire facet of an island falling off or growing up, which may trigger the sudden decay or fast growth of the islands. These processes occur in sufficiently high frequency, they are one of the main mechanisms that leads to the large quantized fluctuation behavior of the islands. This is the motivation for adopting the quantized behavior for the change in island size in our model as described below.

Depending on temperature it might not be feasible to directly observe these island fluctuations from experiments because they occur on a time scale too fast for STM imaging or their amplitude (i.e., number of atoms involved in forming the fluctuation "quantum") might be too small to be measurable. However, in well-designed experiments, we may extract some information by analyzing the area fluctuations. In the initial experiments ($T=205$ K) monitoring the evolution of island areas the acquisition speed was every 100 s because the area selected was large enough to include hundred of islands. Therefore, the area fluctuation of island i in the time interval of $\Delta t=100$ s can be written by the area change of

$$\Delta A_i = A_i(t+\Delta t) - A_i(t), \tag{1}$$

where $A_i(t)$ and $A_i(t+\Delta t)$ are the areas of island i at time t and $t+\Delta t$, respectively. Figure 2 shows the probability distribution of the area fluctuation for all islands in the time interval of 100 s from the experimental STM data. We found that islands with different heights have almost the same probability distributions for smaller area fluctuations but quite different for larger area fluctuation. Since four-layer islands are mostly unstable against coarsening, the probability for area reduction of four-layer islands is large compared to other islands with more layers, as one can see from Fig. 1. For seven-layer islands, however, the situation is reversed, the areas of seven-layer islands grow during coarsening. On the other hand, the probability distribution of area fluctuation is more symmetric for five-layer and six-layer islands, since these islands fluctuate around their initial area sizes during coarsening and their unusual environment remain unchanged. It is interesting that for all islands regardless of their heights, the areas fluctuate with an area unit of about

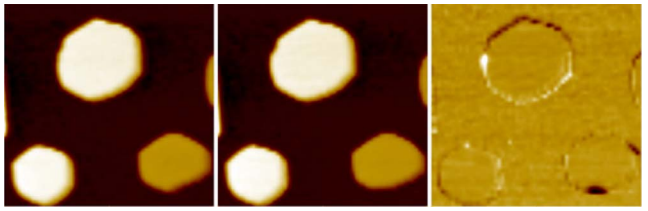

FIG. 3. (Color online) Two successive 237×220 nm^2 images separated by 4 min showing fluctuations of a four-layer island (bottom right) which are 5% its size transferring material from the right to the lower side of the island. The tunneling conditions: −1.5 V and 1 nA. (The temperature is higher 240 K so the islands are bigger and the fluctuations are seen by eye). The third image shows the difference between the two images, where dark area denotes removed material and white area added material. They justify the large quantized fluctuations assumed in the modeling in the current paper.

2 nm^2 in a time interval of $\Delta t=100$ s. This is clearly a collective fluctuation and involves at least ~100 atoms that either attach to or detach from the fluctuating island. On the contrary classical island decay or growth involves the attachment or detachment of single atom. Therefore, it is reasonable to define a minimum unit area A_0 for the evolution of island sizes during coarsening so that the fluctuations of the Pb islands are not due to the attachment or detachment of single atom but are "quantized" in larger units. A_0 is temperature dependent and can become much bigger at higher T.

We considered a Gaussian function to describe the probability distribution for the area fluctuation. However, as shown in Fig. 2(a) with open circles, the Gaussian function can only describe the experimental data well for small area fluctuations. In fact, larger area fluctuations (which are important for the sudden decay of four-layer islands and growth of seven-layer islands) occur more frequently than predicted by the random (uncorrelated) Gaussian distribution. It can be concluded that during coarsening, coordinated processes corresponding to the disappearance or growth of a whole facet plane of the island are important for large area changes.

Figure 3 shows a typical fluctuation for a four-layer island where material is transferred from one side of the island to another side. Although the total island size is almost unchanged this shows how large the material amount that can move in a unit of time. This particular experiment was carried out at higher temperature 240 K and at high flux rate $F=2$ ML/min for deposited amount $\theta=2.7$ ML with acquisition time 4 min. Higher temperature and longer acquisition time were chosen to make the fluctuation larger and visible. It is directly seen from the difference in the two successive images and the magnitude of the area fluctuation is almost an order of magnitude higher as 800 atoms. The image shown is a part of a larger area 1000×1000 nm^2 where many islands tracked have similar fates and this accounts for the long acquisition time of 4 min. We should note that the observations are valid over a wide temperature range (180–250 K over which the seven-layer island height is superstable) and for flux rates sufficiently high ($F\geq2$ ML/min) so that an initial mixture of stable and unstable heights is generated. Island fluctuations have also been observed in the Ag/Si(111) system,[9] which causes shape fluctuations but in Ref. 9 they occur at much higher temperature 500 K with characteristic rings forming at the island edges.

Based on the analysis of experimental data as shown in Fig. 2, we model the probability distribution of quantized area fluctuations $\Delta A=nA_0$ with integer n using an exponential function $f(\Delta A)$ which is expressed as

$$f(\Delta A)=\begin{cases} g(k_+,k_-)e^{-|\Delta A|k_-} & (\Delta A<0) \\ g(k_+,k_-)e^{-|\Delta A|k_+} & (\Delta A>0). \end{cases} \tag{2}$$

$g(k_+,k_-)$ is a normalization factor which is a function of the quantized unit area A_0 and the exponential growth parameter k_+ and decay parameter k_-

$$g(k_+,k_-)=\left(\frac{1}{1-e^{-A_0k_+}}+\frac{1}{1-e^{-A_0k_-}}-1\right)^{-1}. \tag{3}$$

The growth parameter k_+ and the decay parameter k_- are physically related to the island fluctuation. $k_+(k_-)$ determines the probability of area growth (decay) and larger quantity of them means smaller probability of island size grow (decay). For example, at the limit of infinite k_+ there is zero probability for area growth. k_+ and k_- can be determined by fitting the experimental data of the area changes for each island through[13]

$$\langle\Delta A\rangle=A_0\left(\frac{e^{-A_0k_+}}{1-e^{-A_0k_+}}-\frac{e^{-A_0k_-}}{1-e^{-A_0k_-}}\right). \tag{4}$$

The net area fluctuation of each island comes from area growth minus area reduction.

We note that for those stable islands with no obvious growth or decay, the probability distribution of area fluctuation is nearly symmetric for positive and negative fluctuation of islands, so that the absolute values of area fluctuation were used to fit $f(\Delta A)$ as shown in Fig. 2(b). Because of the symmetric feature of the probability distribution, $k_+=k_-=k$, so that Eqs. (2) and (3) become $f(\Delta A)=g(k,k)e^{-|\Delta A|k}$ and $g(k,k)=\frac{1-e^{-A_0k}}{1+e^{-A_0k}}$, respectively. However, we also note that the probability distribution of area fluctuation for those islands with noticeable growth or decay have an exponential factor k_+ or k_- that are different from k. Nevertheless, the exponential constant $k=0.1990$ obtained from the fitting to the fluctuation data from those stable islands with no obvious growth or decay as shown in Fig. 2(b) can be used a guide to determine k_+ and k_-. For the positive area change of $\langle\Delta A\rangle$, we set $k_-=k$, and k_+ can be determined from Eq. (4). On the other hand, for negative $\langle\Delta A\rangle$, we set $k_+=k$, and k_- can be calculated from Eq. (4). If $\langle\Delta A\rangle$ is close to zero, we set $k_+=k_-=k$.

It has been shown that our previous mean-field rate-equation model incorporating quantum-size effect on the chemical potentials of islands describes the average coarsening behavior in Pb/Si(111) system very well.[6,7] Here we also use the same rate equations but incorporate the stochastic process to simulate the coarsening behavior of individual islands with various heights. The area evolution of island i in our previous mean-field quantum coarsening model is described as

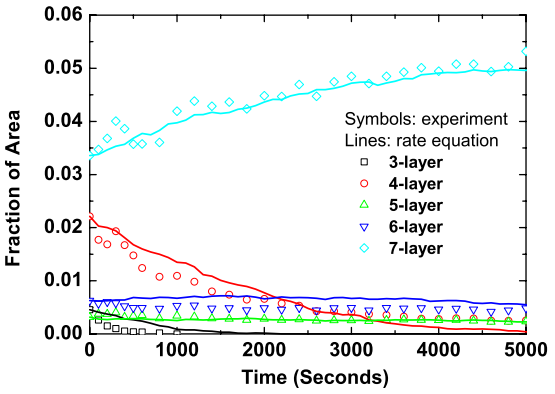

FIG. 4. (Color online) Comparison of average area evolution of islands with different heights obtained from experiments and simulations.

$$\frac{\langle \Delta A \rangle_i}{\Delta t} = 2\pi R_i(\sigma_i^+ - \sigma_i^-), \tag{5}$$

where $\sigma_i^+ = \nu \exp[-(\mu_T - \mu_{WL})/k_B T]$ and $\sigma_i^- = \nu \exp[-(\mu_T - \mu_i)/k_B T]$. μ_{WL} is the chemical potential of wetting layer, μ_T is the chemical potential in transition state, and μ_i is the chemical potential of island i. R_i, ν, k_B, and T are the radius of island i, attempt frequency, Boltzmann constant and temperature, respectively. The chemical potentials of μ_{WL}, μ_T, and μ_i can be obtained in Ref. 6.

In order to incorporate area fluctuations into our coarsening model, the probability distribution function $f(\Delta A_i)$ is used to stochastically determine the area change in each time step. As mentioned above, k_+ and k_- which specify this distribution can be determined according to Eq. (4) by calculating $\langle \Delta A \rangle_i$ which in turn is determined from Eq. (5). The chemical potential in Eq. (5) for stochastic coarsening model will be obtained by fitting the experimentally measured average area evolution of islands with different layers. In our simulation, $\langle \Delta A \rangle_i$ is updated in each time interval of Δt, and meanwhile k_+ and k_- are calculated accordingly. We note that it is necessary to treat positive and negative area fluctuation differently so that the model can capture the growth and decay trend of islands correctly. Regarding the algorithm used to implement this stochastic evolution, a random number r is chosen uniformly distributed on [0,1]. If r is located between $p(A)$ and $p(A+A_0)$, where $p(A) = \Sigma_{B=\infty}^{A} f(B)$, the magnitude of area change ΔA_i will be A.

As one can see from Fig. 4, our stochastic coarsening model can also reproduce the evolution of average area of islands with different layers when the chemical potential at the transition state μ_T is chosen to be 0.66 eV. (The values of the other chemical potentials as a function of height are listed in Ref. 6).

The area evolution of individual islands from the stochastic coarsening model with area fluctuation is shown in Fig. 5. The initial area of individual islands in simulation are the ones determined from the size distribution of the experiment in Fig. 1, and the model input parameters in our simulation are the area fluctuation unit $A_0 = 2$ nm^2 and $\Delta t = 100$ s. Other choice of A_0 does not change the average coarsening behavior shown in Fig. 4 and does not affect the basic fluctuation shape of individual islands either (not shown here). Essentially our model for coarsening of individual islands coupled through the wetting layer captures the main features for evolution of individual islands with different heights observed in our experiments. Preferred height islands are more stable, consistent with observations in our experiments shown in Fig. 1. During coarsening, the areas of islands fluctuate. In the presence of these fluctuations, some islands are stable, while some decay. For four-layer islands although the initial areas are almost the same, the coarsening behavior is quite different. Most four-layer islands decay and suddenly disappear but a few still survive during the simulation time. This behavior is different from the mean-field coarsening model where all four-layer islands behave in a similar way, decaying and disappearing quickly.[6] Thus the coarsening behavior of four-layer islands in the mean-field model depends only on their initial lateral sizes. However, in the present stochastic coarsening model with area fluctuation, a few four-layer islands survive during coarsening. For the few five-layer, six-layer, and the far more abundant superstable seven-layer islands, they persist, so fewer islands decay during coarsening, but note that when they decay, they also disappear in similar sudden death mode.

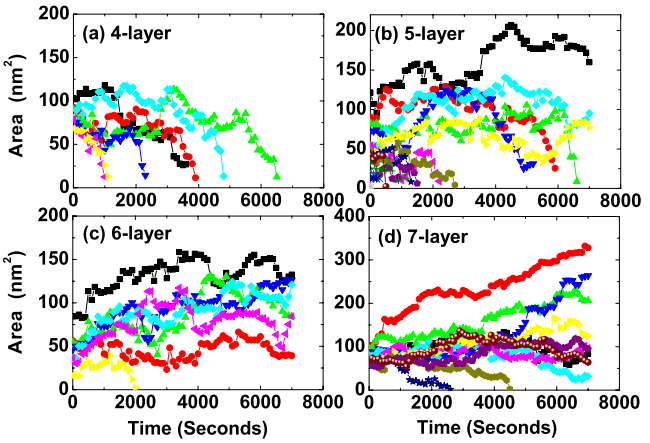

FIG. 5. (Color online) Time evolution of individual islands with (a) four layers, (b) five layers, (c) six layers, and (d) seven layers from the simulation of stochastic coarsening model.

In summary, a stochastic coarsening model with collective fluctuation effect of individual islands coupled through the wetting layer incorporated is developed to study the area evolution of individual Pb islands with different heights on Si(111) surface. Fluctuations are quantized built from the concerted and correlated motion of many atoms that move collectively with the same time constant. Our model reproduces the observed area fluctuation of islands and sudden death of individual small islands observed in STM experiments. Our results indicate that the classical picture of coarsening based on attachment and detachment of individual islands and the smooth dependence of the island decay is dramatically modified in systems driven by quantum size effects and it can partially account for the fast and unusual degree of the Pb/Si(111) self organization.

Work at Ames Laboratory was supported by the U.S. Department of Energy, Basic Energy Sciences, including a grant of computer time at the National Energy Research Supercomputing Centre (NERSC) in Berkeley, under Contract No. DE-AC02-07CH11358. M.L. was supported by NSF of China under Grant No. 10704088. J.E. was supported by NSF under Grant No. CHE-0809472.

[1] L. Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Material Processing* (Springer, Berlin, 2001).

[2] M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, Surf. Sci. Rep. **16**, 377 (1992).

[3] P. A. Thiel, M. Shen, D.-J. Liu, and J. W. Evans, J. Phys. Chem. C **113**, 5047 (2009).

[4] C. A. Jeffrey, E. H. Conrad, R. Feng, M. Hupalo, C. Kim, P. J. Ryan, P. F. Miceli, and M. C. Tringides, Phys. Rev. Lett. **96**, 106105 (2006).

[5] M. Hupalo and M. C. Tringides, Phys. Rev. B **75**, 235443 (2007).

[6] M. Li, J. W. Evans, C. Z. Wang, M. Hupalo, M. C. Tringides, and K. M. Ho, Surf. Sci. **601**, L140 (2007).

[7] M. Li, C. Z. Wang, J. W. Evans, M. Hupalo, M. C. Tringides, and K. M. Ho, Phys. Rev. B **79**, 113404 (2009).

[8] K. L. Man, M. C. Tringides, M. M. T. Loy, and M. S. Altman, Phys. Rev. Lett. **101**, 226102 (2008).

[9] *Surface Diffusion: Atomistic and Collective Processes*, edited by M. C. Tringides (Plenum, New York, 1997).

[10] J. G. McLean, B. Krishnamachari, D. R. Peale, E. Chason, J. P. Sethna, and B. H. Cooper, Phys. Rev. B **55**, 1811 (1997).

[11] P. Wynblatt and N. A. Gjostein, Prog. Solid State Chem. **9**, 21 (1975).

[12] K. Morgenstern, G. Rosenfeld, E. Laegsgaard, F. Besenbacher, and G. Comsa, Phys. Rev. Lett. **80**, 556 (1998).

[13] For small islands, the probability of disappearance is $\Sigma_{\Delta A<-A} f(\Delta A)$. Here A is the island area. In calculation, the mean value of area $\langle \Delta A \rangle = \Sigma_{\Delta A<-\infty}^{\infty} \Delta A f(\Delta A)$ fluctuation is used, as the probability of the area reduction larger than A is almost very small and thereby it is unnecessary to modify the form of $\langle \Delta A \rangle$. If $\Delta A < -A$ is selected according to the selection rule described below, the island disappears.