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Competition between area and height evolution of Pb islands on a Si(111) surface

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Scanning tunneling microscopy experiments reveal that small Pb islands with unstable heights, e.g., four layers, on a Si(111) surface decay during coarsening, whereas large islands do not decay but grow to a stable height. This bifurcation in evolution is analyzed by incorporating quantum size effects into theoretical models for island growth dynamics with appropriate geometries. The *effective* energy barrier for Pb atoms to reach the top of four-layer islands is estimated at about 0.26 eV.

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I. INTRODUCTION

In recent years, many intriguing features have been discovered in epitaxial growth of Pb islands on a Si(111) surface. Pb islands grow to specific heights which are particularly stable[1] due to "quantum size effects" (QSE) associated with electron confinement in the vertical direction within the islands.[2–5] However, a detailed understanding of the kinetics of island formation and evolution, which is influenced by QSE, is still lacking.

Recently, rapid coarsening of Pb islands on a Si(111) surface has been observed.[6] Islands with unstable height decay quickly without changing their heights. Furthermore, the coarsening kinetics has a strong and unusual dependence on the deposition flux (which controls the initial island distribution) in contrast to classical coarsening.[7] To explain this behavior, we developed a theoretical model which incorporates QSE generating a strong height-dependent driving force for coarsening. It also accounted for the role of wetting layer which acts as an efficient mass transport medium between islands.[8] In this model, evolution in island height was not considered.

However, further scanning tunneling microscopy (STM) experiments[9] found that an unstable island will not decay if its lateral size is large enough, but rather evolve to a stable height. Figure 1 shows evolution at $T=190$ K of a large four-layer island of radius ~80 nm with a five-layer-high ring around the perimeter. Large islands were formed by an initial deposition at 240 K with coverage of 1.75 monolayer (ML). The surface was then cooled to 180 K, and a second deposition of 0.25 ML was used to generate smaller islands mainly on the wetting layer between the large islands and to trigger the coarsening of islands to stable heights.[9] More detailed analysis reveals that ring growth is due to diffusion of Pb atoms from the wetting layer to the top of four-layer islands with a climbing rate of ~ 1.8 atoms/s at 190 K.[9]

In this paper, in order to investigate the bifurcation between island evolution in area versus height, we extend the previous theoretical model[8] to describe the competition between area and height evolution in terms of relevant partial chemical potentials. Below, we first describe the model energetics determining these chemical potentials and then describe the model dynamics. Predicted island evolution is in good agreement with experiments. The temperature dependence of the predicted rate of Pb atoms to reach the top of four-layer islands is described by an *effective* energy barrier of ~ 0.26 eV, consistent with an experimental estimate.[9,10]

II. MODEL GEOMETRIES AND ENERGETICS

Figure 2 shows the island geometries adopted in our three different models for island evolution. The first is the most idealized, assuming that islands are perfect cylindrical mesas with continuously changing height as shown in Fig. 2(a). The other two models incorporate a more realistic description of the formation of new higher layers as shown in Figs. 2(b) and 2(c), respectively. Below, we first specify the relevant total free energies for each of these island geometries. We also introduce "partial" chemical potentials, $\mu(\alpha)$, for each possible growth mode α, which are defined as the change in free energy of the island for each atom added in that specific growth mode. The lower $\mu(\alpha)$, the more favorable is growth mode α. A "growth index function" is defined as the difference between partial chemical potentials for two modes indicating the preferred mode.

A. Uniform height growth model

Pb islands on Si(111) of interest here tend to be three-dimensional with flat tops and steep side walls. Thus, in our simplest geometric model, they are approximated as circular

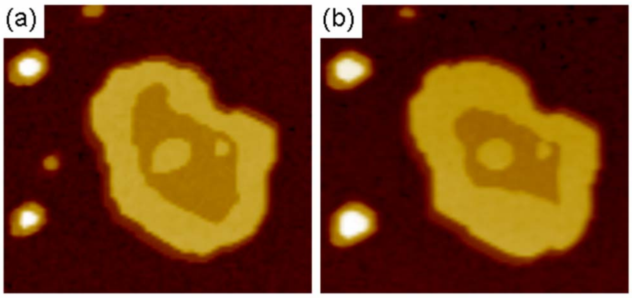

FIG. 1. (Color online) STM images (98×84 nm^2) of a large four-layer Pb island with a five-layer-high ring around its periphery at $T=190$ K. Image (b) is taken 92 min after (a).

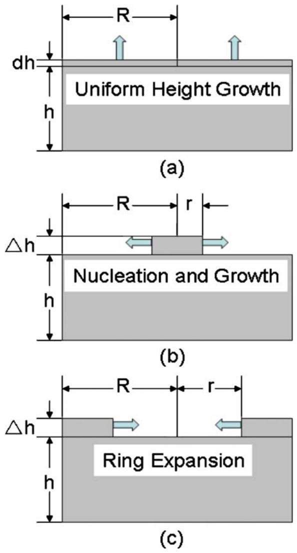

FIG. 2. (Color online) Schematic of the cross section of island geometries for various models: (a) uniform height growth; (b) island nucleation and growth (on top of unstable islands); (c) ring expansion (after formation of a ring on top of unstable islands around the periphery).

mesas with radii R and heights h above the wetting layer. The volume of the island is $V \approx \pi R^2 h$ and the number of atoms is $N = V/\Omega$, where Ω is the atomic volume. Units of h are interlayer spacing and for R are chosen so that πR^2 gives the number of atoms in each layer and $\Omega = 1$. The free energy of an island can be written as[8]

$$E(R,h) = \pi R^2 h \epsilon_b + \pi R^2 \gamma_t(h) + 2\pi R h \gamma_s. \tag{1}$$

Here, ϵ_b is the bulk energy per unit volume; γ_t and γ_s are the surface energies per unit area of the mesa top and the mesa sidewall, respectively. Based on density-functional theory analysis[4,11] and experimental observations,[1,3] we obtain $\gamma_t \approx 0.183$, 0.196, 0.191, 0.201, and 0.192 eV for $h = 3$, 4, 5, 6, and 7, respectively; γ_s is estimated to be 0.33 eV.[8,12]

Then, the partial chemical potential for radial growth satisfies[8,13]

$$\mu(R) = \Omega \left. \frac{dE}{dV} \right|_{h=\text{const}} = \Omega \left(\epsilon_b + \frac{\gamma_t}{h} + \frac{\gamma_s}{R} \right). \tag{2}$$

For height growth, the partial chemical potential satisfies[13]

$$\mu(h) = \Omega \left. \frac{dE}{dV} \right|_{R=\text{const}} = \Omega \left(\epsilon_b + \frac{d\gamma_t}{dh} + \frac{2\gamma_s}{R} \right). \tag{3}$$

Here we will assume that γ_t is a continuous function of h and linearly interpolates the two relevant discrete heights. Thus, one has $d\gamma_t/dh = \Delta\gamma_t/\Delta h$, where $\Delta\gamma_t = \gamma_t(h+\Delta h) - \gamma_t(h)$ with $\Delta h(=1$ or $2)$ denoting the discrete incremental height increase.

The growth index function, $\Delta\mu = \mu(h) - \mu(R)$, reflects the competition between radial growth $(\Delta\mu > 0)$ and growth in height $(\Delta\mu < 0)$ of a Pb island. If the island radius R is large enough, the third terms on the right side in Eqs. (2) and (3) can be neglected. Then $\Delta\mu$ is simply determined from knowledge of γ_t versus h and is invariably negative, e.g., $\Delta\mu = -0.055(-0.047)$ for growth from $h=4$ to 5 (6) and -0.028 (-0.036) for growth from $h=5$ to 6 (7). Therefore, in this simplest geometric model, an island with large lateral size energetically prefers to grow in height, consistent with our experimental observations.[9] A large four-layer island tends to grow to five layers. But a large five-layer island tends to simultaneously grow two layers to become seven-layer high because of an additional energetic preference over growth to six-layer high. This could explain the bilayer growth from five-layer to seven-layer islands observed in experiments.[10]

For an island with smaller radius, however, the third terms in Eq. (2) and (3) cannot be ignored. Such islands may decay slowly or disappear quickly within 2–3 min.[8] Whether a relatively small island grows in area, in height, or in both directions simultaneously depends on its lateral size.

B. Island nucleation and growth model

In reality, growth of island height occurs by nucleation of new islands on top of an unstable island. Formation of the new island could occur in the center of the unstable island, but more often off center. The analysis below applies in either case, at least until the new island grows to reach the edge of the lower layer. For the island geometry in Fig. 2(b), the energy of the island can be written as

$$\begin{aligned} E(R,h,r,\Delta h) = {} & (\pi R^2 h + \pi r^2 \Delta h)\epsilon_b + \pi (R^2 - r^2)\gamma_t(h) \\ & + \pi r^2 \gamma_t(h+\Delta h) + 2\pi R h \gamma_s + 2\pi r \Delta h \gamma_s . \end{aligned} \tag{4}$$

The partial chemical potentials for radial growth of the base island and new top layer, respectively, have the form

$$\mu(R) = \Omega \left(\epsilon_b + \frac{\gamma_t(h)}{h} + \frac{\gamma_s}{R} \right), \tag{5}$$

$$\mu(r) = \Omega \left(\epsilon_b + \frac{\Delta\gamma_t}{\Delta h} + \frac{\gamma_s}{r} \right). \tag{6}$$

In this model when r is very small, the partial chemical potential for growth of a new island will be much higher than that for radial growth of the base. Clearly, there is a significant barrier to nucleate such islands and they must be sufficiently large to survive. For example, for a four-layer island with very large R, the radius of atop layer island must exceed $r=6$ in order to favor its growth (based on the parameters indicated above). The smaller islands on top of large four-layer islands as shown in Fig. 1 were formed during the second stage of deposition. They are large enough to survive, their size not changing significantly over 92 min.

C. Ring expansion model

As observed in the experiments, a ring structure forms quickly along edges on top of a large four-layer island. Subsequently, the ring gradually expands.[9] For the model geometry shown in Fig. 2(c) with the ring height, $\Delta h(=1)$, the free energy can be written as

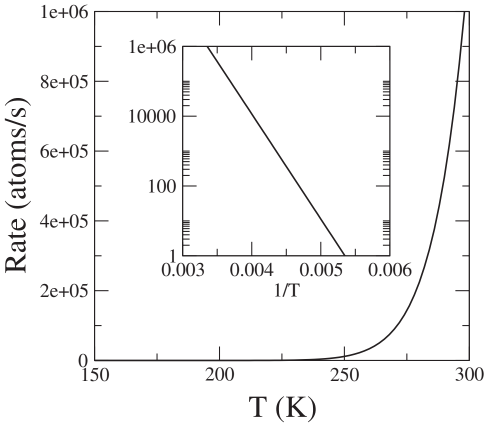

FIG. 3. Temperature dependence of diffusion rate of Pb atoms from the wetting layer to the top of a large four-layer island with $R=80$ nm. Inset shows log plot of rate vs $1/T$.

$$\begin{aligned}E(R,h,r,\Delta h) &= [\pi R^2 h + \pi(R^2 - r^2)\Delta h]\epsilon_b + \pi R^2 \gamma_t(h)\\ &\quad + \pi(R^2 - r^2)\gamma_t(h+\Delta h)\\ &\quad + 2\pi R(h+\Delta h)\gamma_s + 2\pi r \Delta h \gamma_s. \qquad (7)\end{aligned}$$

The partial chemical potentials for radial growth and ring expansion, respectively, satisfy

$$\mu(R) = \Omega\left(\epsilon_b + \frac{\gamma_t(h+\Delta h)}{h+\Delta h} + \frac{\gamma_s}{R}\right), \qquad (8)$$

$$\mu(r) = \Omega\left(\epsilon_b + \frac{\Delta \gamma_t}{\Delta h} - \frac{\gamma_s}{r}\right). \qquad (9)$$

The growth index function, $\Delta\mu=\mu(r)-\mu(R)$, is always negative, so that ring expansion is always energetically favorable. Thus, for a four-layer island, once a ring structure is formed on top, it will always expand.

III. MODEL DYNAMICS

Next, we give a general specification of island evolution in the various specific growth modes, α, for the above models. The rate of change in size, N (measured in number of atoms), associated with growth mode α satisfies

$$dN/dt|_\alpha \approx L_\alpha(\sigma_\alpha^+ - \sigma_\alpha^-). \qquad (10)$$

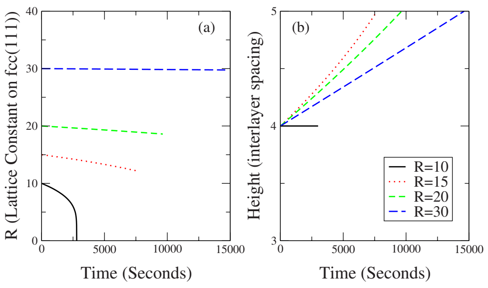

FIG. 4. (Color online) (a) Time evolution of the area and (b) height of a four-layer island with different initial radius $R=10$, 15, 20, and 30, respectively, at $T=190$ K in uniform height growth model.

In uniform height growth model, $\alpha=R$ (radial growth) or h (height growth) and in the other two models, $\alpha=R$ (radial growth of the base) or r (island growth or ring expansion). Also, L_α denotes the length of the step edge from which adatoms attach and detach for growth in mode α. In Eq. (10), $\sigma_\alpha^+=\nu_0 \exp[-(\mu_\alpha^T-\mu_{\rm WL})/(k_B T)]$ and $\sigma_\alpha^-=\nu_0 \exp\{-[\mu_\alpha^T-\mu(\alpha)]/(k_B T)\}$, representing adatom attachment and detachment rates (per unit length), respectively. We further assume that adatoms are attaching to islands from the wetting layer which has a chemical potential $\mu_{\rm WL}$. In these expressions, $\mu(\alpha)$ are the above-mentioned partial chemical potentials, μ_α^T is the chemical potential in the transition state, ν_0 is attempt frequency taken as $10^{13}/s$, T is the surface temperature, and k_B is the Boltzmann constant.

Model analysis follows from integrating Eq. (10) after prescribing the initial island configuration. We assume that the chemical potential of the wetting layer, $\mu_{\rm WL}$ ~ 0.040 eV,[8] does not change during evolution of the island of interest. The size of the region influencing island evolution is very large (1000×1000 nm^2), so that the wetting-layer coverage which controls $\mu_{\rm WL}$ will not change much by removing $\sim$10 000 atoms during island evolution.

A. Uniform height growth model

In this case, Eq. (10) can be written as

$$h\frac{dR}{dt} = (\sigma_R^+ - \sigma_R^-), \quad R\frac{dh}{dt} = 2(\sigma_h^+ - \sigma_h^-), \qquad (11)$$

for radius and height growth. We choose $\mu_R^T\sim 0.66$ eV as previously,[8] but need to estimate μ_h^T.

As noted above, the experimental rate of Pb atoms reaching the top of a four-layer island with $R\approx 80$ nm is $\sim$1.8 atoms/s at $T=190$ K. Using Eq. (11), μ_h^T must be chosen as 0.66 eV to match this rate. Then, from Eq. (11), we can calculate the transfer rate of Pb atoms from the wetting layer to the top of the island at various temperatures, revealing a strong temperature dependence (see Fig. 3). At 180 K, the estimated transfer rate is about 0.24 atoms/s, but at 240 K it increases to about 3655 atoms/s. This analysis explains why in STM experiments there is no visible change on the top of the islands at 180 K, but at 240 K the change cannot be observed within the STM acquisition speed.

The inset of Fig. 3 shows an Arrhenius plot determining the *effective* energy barrier of about 0.26 eV which Pb atoms in the wetting layer must overcome to reach the top of four-layer islands. This is consistent with calculations of the modified embedded atom method.[14] In the previous experiments[10] the effective energy barrier was estimated $\sim$0.32 eV for Pb atoms to reach the top of five-layer islands and form seven-layer islands. This barrier should be smaller for unstable islands.

For smaller islands, the areas and the heights change simultaneously. Using the uniform height growth model, we simulate the evolution of four-layer islands with various initial radii (see Fig. 4). An island with $R=10$ decays in area very quickly, keeping its height unchanged. In contrast, for an island with $R=30$, the lateral size barely changes, but height increases. For the island with $R=15$ and 20, the area and height change simultaneously with area shrinking and height growing to quickly reach five layers. The "minimum" radius R for a four-layer island that does not disappear is estimated about 3.5 nm at 190 K. If R is bigger than ~ 11.5 nm, the area does not change, but height grows. After the island reaches five layers, it may grow up to seven-layer islands over longer times. The above analysis shows that predictions of the uniform height growth model are consistent with the experimental observations.

B. Ring expansion model

We have also investigated the evolution of base area and ring for a four-layer island with a ring in this model where Eq. (10) becomes

$$(h+\Delta h)\frac{dR}{dt}=(\sigma_R^+-\sigma_R^-), \qquad -r\Delta h\frac{dr}{dt}=(\sigma_r^+-\sigma_r^-). \quad (12)$$

All parameters are kept the same as those in the uniform height growth model including $\mu_R^T \sim 0.66$ eV and we select $\mu_r^T \sim 0.66$ eV based on the same type of analysis as for the uniform height growth model.

Figure 5 shows the time evolution of island radius R, inner radius r of the ring, and the average height of the island. The latter is readily determined from $\langle h\rangle = [hr^2+(h+\Delta h)(R^2-r^2)]/R^2$. The evolution of islands is qualitatively similar to that in the uniform height growth model. However, since the ring expansion model accounts for the detailed geometry of the ring structure, so there are slight differences. For example, for islands with initial radius larger than 20, R increases slightly during coarsening, in contrast to the behavior in uniform height growth model. The island with $R=10$ decays and quickly disappears in uniform height growth model, while it survives in the ring expansion model. This is because once a ring is formed on top of a four-layer island, the ring growth is preferred, and a new layer is formed quickly, and finally the island grows to a stable height before it disappears.

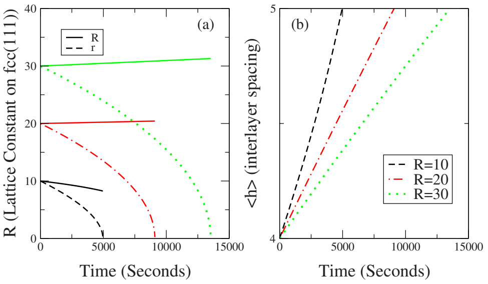

FIG. 5. (Color online) (a) Time evolution of the island radius R and inner radius of the ring r for a four-layer island with different initial radii $(R=r)$ in ring expansion model at $T=190$ K. (b) Time evolution of the average height $\langle h\rangle$.

In summary, the competition between growth of island area and height was investigated using various models for island geometry evolution. Detailed analysis indicates the existence of a significant barrier for nucleation of new islands on top of islands with unstable heights. Furthermore, such unstable islands must be sufficiently large to avoid rapid decay. However, once a ring structure has formed on such islands, it is energetically more favorable for the ring to expand (increasing the average island height) than for radial growth of the supporting island.

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