Quantum Size Effect on the Diffusion Barriers and Growth Morphology of Pb/Si(111)

T.-L. Chan, C. Z. Wang, M. Hupalo, M. C. Tringides, and K. M. Ho

Ames Laboratory-United States Department of Energy and Department of Physics and Astronomy, Iowa State University,
Ames, Iowa 50011, USA

An intriguing growth morphology of Pb islands on a Si(111) surface is observed in our STM experiments: the growth of a Pb layer on Pb islands with unstable heights starts from the periphery and moves towards the center, while the nucleation of the next layer on stable Pb islands starts away from the periphery. Using first-principles total energy calculations, we have studied the diffusion barriers of Pb adatoms on a freestanding Pb(111) film as a function of film thickness. The diffusion barriers are found to be very low ($<$60 meV), and a bi-layer oscillation due to the quantum size effect (QSE) is observed, with a lower barrier on the odd-layered, relatively unstable Pb films. The diffusion barrier difference between the odd- and even-layered film is as large as 40 meV. The observed unusual growth can be attributed to this big difference in the diffusion barriers due to QSE.

The ability to manipulate atoms to form regular nanostructures is strongly pursued nowadays, and a popular technique to achieve such a goal is through the self-assembly. For metallic nanostructures, quantum size effects have been recently recognized as a strong driving force for self-assembly because the size-dependence of the energetic stability of the structure can be used to select certain preferred sizes and geometry of the film in the deposition process [1–8]. While quantum size effects on the energy stability of thin films is well studied, quantum size effects in the kinetics is equally important in explaining the observed extraordinary efficiency of the system in forming metallic islands of selective heights with flat tops and steep edges on the semiconductor surfaces at quite low temperatures. This must involve very fast kinetics that cannot be explained by existing film growth models [9].

In this Letter, we investigate the quantum size effects on the growth kinetics and morphology of metal on semiconductor surfaces using Pb/Si(111) as a prototype system. We observed an unusual growth morphology of Pb islands on Si(111) surface in which islands with stable and unstable heights exhibit different growth behavior. The growth of a new layer on unstable islands shows a ring at the island perimeter propagating towards the island center. To our knowledge, this is the first time that an intermediate state before the completion of the island during the growth of Pb islands on Si(111) has been captured experimentally, and this novel ring morphology cannot be explained within the conventional picture by the competition between terrace diffusion vs interlayer diffusion [10]. Using first-principles total energy calculations, we have studied the diffusion of Pb atoms on Pb(111) film. Our calculation indicates that this collective growth behavior has a microscopic origin from the quantum size effect on the diffusion barriers.

Figure 1 shows an STM topography image of an intermediate transient configuration of Pb/Si(111) with several island heights present, both stable and unstable, evolving towards a distribution which eventually will include only stable heights. The initial morphology (not shown) was generated by depositing 1.6 ML of Pb on top of the Si(111) $\alpha - \sqrt{3} \times \sqrt{3}$ phase at 180 K. At this temperature, laterally extended 3-layer islands with respect to the Si(111) substrate (i.e., 2-layer islands with respect to the wetting layer) are observed first. This is the first stable height for growth on this interface followed by 6-layer islands as the next stable height when the height evolution is completed. With further Pb deposition, stable heights differing by bilayer increments are observed. On this initial 1.6 ML distribution of Pb islands of average lateral size of 100 nm, an additional amount of 1.3 ML is deposited. The islands have irregular shapes because most of them initially grow from coalescence events with separate islands merging without shape rearrangement. This shows that very fast terrace diffusion is competing with much slower edge diffusion. The outcome of this additional deposition is shown in Fig. 1. Mostly 6-layer islands are formed, but a few uncovered areas of 5-layer islands still exist. In a few cases, we also observe the beginning of the formation of 7-layer islands on top of the incomplete 6-layer islands.

We found that less than 15% of the 6-layer islands are covered, far below the estimated 0.5 ML amount deposited on the almost completed 6-layer islands; i.e., less than half of the deposited amount remains on top of the 6-layer islands. The corresponding number for stable layers covering unstable height islands is 85%. This can be understood by the Pb atoms on the stable 6-layer Pb islands more likely to diffuse to lower layers to increase the lateral dimension of the islands rather than building the next layer to form an unstable thickness, while Pb atoms on the unstable islands will tend to remain on the top to build the next stable layer. Therefore, it can be implied that stable Pb islands have a lower Ehrlich-Schwoebel (E-S) barrier at the edge of the islands, while the reverse is true for unstable islands.

The most striking feature of the image is the very unusual growth morphology where all the 6-layer islands
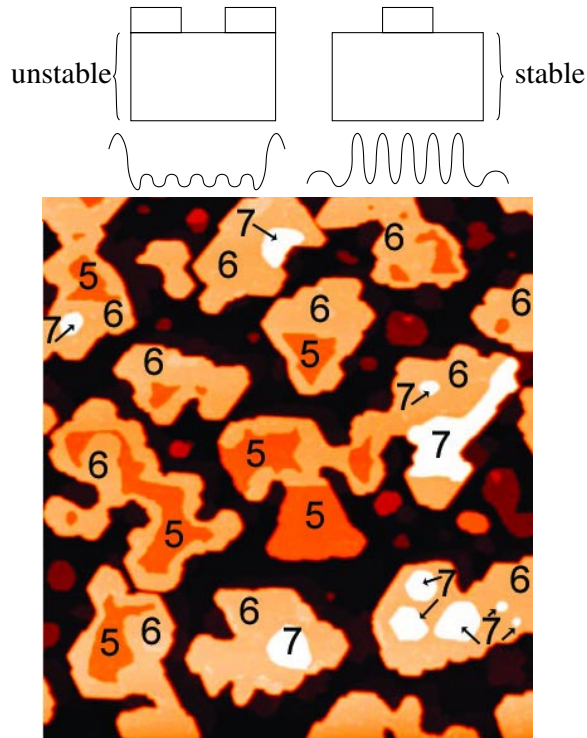
FIG. 1 (color online). Top: A schematic diagram illustrating the potential energy surface and growth morphology on stable versus unstable islands. An additional layer on stable islands grows from the center while the growth is from the periphery for unstable islands. Bottom: An STM image of 330 nm × 370 nm with a total Pb coverage of 2.9 ML at 180 K on Si(111) $\alpha - \sqrt{3} \times \sqrt{3}$ phase formed by stepwise deposition (i.e., 1.3 ML on top of already 1.6 ML island distribution). The numbers label the island height measured from the Si(111) substrate.

complete their top by growing from the perimeter towards the center with almost constant width. The growing front follows the shape of the initial 5-layer island perimeter. On the other hand, the growth of the unstable 7-layer islands shown as white regions on the 6-layer stable islands is by nucleating small compact islands at the island center. Only in one case the 7-layer island (center right) seems to co-alesce into a single extended island possibly because of the narrow "neck" at the triangularly shaped bottom part.

To understand this unusual growth morphology, we have studied the diffusion for a Pb adatom on Pb films as a function of film thickness using first-principles total energy calculations. Our calculations are carried out using the VASP [11] program which is based on first-principles density-functional theory [12]. We used ultrasoft pseudo-potential [13] and plane waves basis with an energy cutoff of 144 eV. Scalar relativistic effects are included and the generalized gradient approximation (PW-91) [14] is used for the electronic exchange-correlation energy functional. A Monkhorst-Pack grid [15] of 4 × 4 × 1 is used for the Brillouin-zone integration. A 4 × 4 unit cell is used for the Pb film, and the thickness of the film varies from 3 to 9 Pb layers in our calculations. 12 Å of vacuum space is in-

cluded in our supercell. The bottom layer of the Pb film is kept fixed, while the rest of the Pb atoms are allowed to relax.

We validate our setup described above by calculating the surface energy for freestanding Pb(111) film from 3 layers up to 9 layers. The surface energy is calculated using $E_s = (E_{\text{film}} - n \times E_{\text{Pb}})/2$, where E_{film} is the total energy of the Pb film, n is the number of Pb atoms in the system, and E_{Pb} is the energy of a Pb atom in its crystalline fcc structure. The results, shown in Fig. 2(a), agree well with previous first-principles study of Ref. [5] which exhibits a bilayer oscillation due to quantum size effect (QSE). The experi-mentally observed stable heights below 5 layers are differ-ent from the calculated results using freestanding Pb film because the electronic phase shift at the Pb/Si interface is not accounted in calculations. However, our calculation and experiment on the stable heights agree with each other for thicker films. In order to map out the potential energy surface for Pb atom diffusion, we place a Pb adatom on different positions of a grid mesh over the Pb(111) film. The Pb adatom is allowed to adjust its height, but not its coordinates parallel to the Pb(111) surface. All other Pb atoms in the Pb film are allowed to fully relax except the bottom layer. These calculations are carried out for Pb(111) films from 3 to 9 atomic layers. Our results show that, except for the 3-layer film, the hcp site as indicated in Fig. 3 is the lowest energy location for the Pb adatom, while the fcc site is the saddle point in the diffusion pathway for the Pb adatom from one cell to
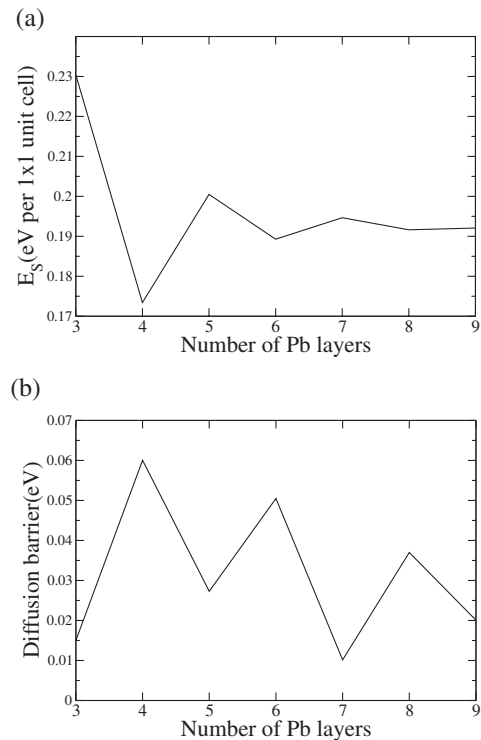

FIG. 2. (a) The surface energy per 1 × 1 unit cell of a free-standing Pb film from 3 to 9 atomic layers; (b) The diffusion barrier of a Pb adatom on a 3- to 9-layer Pb film.
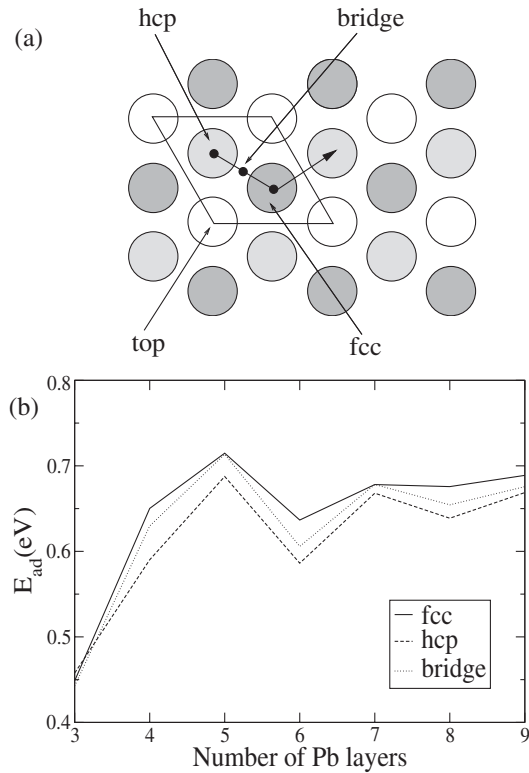
FIG. 3. (a) Diffusion pathway of a Pb adatom on a Pb film. Only the top three Pb layers are shown, with the first, second, and third layer shaded white, light gray, and dark gray, respectively. A 1×1 unit cell is outlined to illustrate the diffusion of a Pb adatom from one unit cell to another; (b) The adsorption energies of a Pb adatom on a 3- to 9-layer Pb film at fcc (solid line), hcp (dashed line) and bridge site (dotted line).

another. The bridge site (the midpoint between the hcp site and fcc site) has an energy in between the lowest energy hcp site and the fcc saddle point (except the 3-layer film). For 3-layer Pb film, the lowest energy site for a Pb adatom is at the bridge site, and the saddle point shifted to the hcp site as well. For all Pb films, the top sites are the maxima of the potential energy surface.

The adsorption energies of the Pb adatom are plotted in Fig. 3(b). The adsorption energy E_{ad} is defined as $E_{ad} = E - E_{film} - E_{Pb}$, where E is the total energy of the whole system containing both the Pb adatom and the film, and E_{Pb} is the energy of a Pb atom in its crystalline fcc structure. E_{film} is the total energy of the previously optimized Pb film of the same thickness without adatoms. A bilayer oscillation of the adsorption energies can be seen from Fig. 3(b), similar to the behavior of the surface energies of a freestanding Pb(111) film.

With the exception of the 3-layer Pb film, the energy barrier for a Pb adatom diffusing on the Pb(111) film is the energy difference between the fcc and the hcp site. The diffusion barriers as a function of film thickness from 3- to 9-layer Pb(111) film is plotted in Fig. 2(b). Our results show that the energy barrier for a Pb adatom diffusing on the surface of a Pb(111) film is very small, ranging from 10 to 60 meV or even smaller (less than 40 meV when the film is more than 7 layers thick). This result may explain the fast growth of Pb islands on Si(111) surface at low temperature (~180 K). It is interesting to note that the diffusion energy barriers also exhibit a bilayer oscillatory behavior, due to the QSE. The oscillation in the diffusion barrier anticorrelate with that in the surface energy. For those film thickness that has lower surface energy (stable films) the diffusion barrier is higher, and vice versa. The ratio between the energy barrier for stable and unstable films is as large as 6 (4 on average). We believe that the diffusion barrier of a Pb adatom on Pb island on Si(111) should be very similar to that on a freestanding Pb(111) film, as long as the Pb islands are more than 5 layers high.

The unusual growth morphology, especially the difference between nucleation on top of stable versus unstable islands, for Pb islands on Si(111) observed in the STM experiment can be attributed to the large oscillation in the diffusion barrier between the stable and unstable Pb films. Another contributing factor is the E-S barriers at the edge of the Pb island. However, to calculate the E-S barriers for Pb/Si(111) is still beyond our current capability because a huge unit cell is required such that QSE as a function of the island height is not affected by QSE due to the width of the island in the modeling. Nevertheless, our experiments qualitatively show that E-S barrier for the Pb island with stable height is much lower than that for the island with unstable height. A schematic diagram for the energy landscape on top of the two types of Pb islands is shown at the top of Fig. 1. According to this schematic plot, Pb adatoms deposited on stable Pb islands may encounter other deposited Pb adatoms to nucleate an island of next height before diffusing to the edge of the islands due to the higher diffusion barrier. In addition, Pb adatoms close to the periphery of the stable Pb islands tend to diffuse to lower layers to increase the lateral dimension of the islands due to low barriers at step edge precluding any growth on top of stable films near the edge. On the other hand, Pb adatoms deposited on unstable Pb islands experience a low diffusion barrier throughout the island top, but they will be retained on the top due to the high step edge barrier and nucleate the next layer if the step edge barrier is nonreflecting [16]. This growth picture is further elaborated by the analysis of initial nucleation process as follows.

The probability of two consecutive Pb adatoms landing on top of an island of size L nucleating with each other without diffusing to the island edge can be calculated by $P = \int_0^\infty P_1(t)P_2(t)dt$, where $P_1(t)$ is the probability for the first Pb adatom to remain on top of the island at time t, and $P_2(t)$ is the probability of the second Pb adatom to land on the island and within the radius of the capture basin l around the first adatom at time t. The probability of the second adatom landing on the island at a certain time is governed by the Poisson statistics with the average time interval between two consecutive incoming Pb adatoms being $1/F(l/a_0)^2$, where F is the deposition rate and

$(l/a_0)^2$ is the number of sites on the island within the radius l. If the second adatom does not land close to the first one, the probability for them to meet each other is assumed to be very small, then these two Pb adatoms are likely to diffuse out of the stable island or nucleate at the edge of the unstable islands. By using $F = 1 \text{ ML}/\min$, a typical island size of $L = 100$ nm, a temperature of 180 K and $l = 15$ nm (about half of the distance between two of the three nucleated 7-layer islands in the bottom right of Fig. 1), P is found to be 3×10^{-5} for a stable island with a diffusion barrier $E = 0.05$ eV, while $P = 4 \times 10^{-6}$ for unstable height Pb island with $E = 0.015$ eV. On the other hand, after depositing 0.5 ML (out of the total 1.3 ML), there will be approximately 4×10^4 Pb adatoms landing on the 100 nm $\times$ 100 nm Pb island. Although the probability is small for two consecutive Pb adatoms meeting each other without diffusing to the edge, the probability for the two Pb adatoms to meet after 4×10^4 attempts can be significant. Our calculations show that there is a probability of 75% (16%) for two successively deposited Pb adatoms to meet each other without diffusing to the edge after depositing 0.5 ML on stable (unstable) height island. This nucleation probability is a measure of possible island nucleation close to the center of the island. Hence, our calculations illustrate that nucleating a Pb layer close to the center of a stable Pb island top is more probable than on unstable island. Our analytic estimate of the nucleation probability on top of stable islands and the choice of $l = 15$ nm is fully supported by analytic work and detailed Monte Carlo simulations of the second layer nucleation process in the literature [17–19]. In Ref. [18], the second layer nucleation on top of an island of size R was studied as a function of D/F (D is diffusion coefficient) and the step edge barrier $\Delta E_s/kT$. Nucleation is only observed for island size of at least $R_{\min} = 100$ nm. We found according to Fig. 2 of Ref. [18] and using $D/F = 10^{12}$ derived from our calculated D and the experimental F that second layer nucleation at this minimum island size $R_{\min}$ is only possible for step edge barrier less than 0.08 eV, which is small and agrees with the estimate from our experiment. For unstable island, most of the Pb adatoms diffuse to the edge of the island without meeting other deposited Pb adatoms on their way and nucleate at the edge of the island as discussed previously. Once nucleation starts at the edge, Pb atoms will adsorb at the island edge and further reduce the probability to nucleate at the center because of the very fast diffusion.

In summary, we observed a dramatic and unconventional growth mode of Pb islands on Si(111) by STM experiments: the growth of an additional layer on a stable Pb island starts from the center while it starts from the periphery for unstable Pb island. The diffusion barriers of a Pb adatom on 3- to 9-layer freestanding Pb film are calculated by first-principles calculations. The surface energies, adsorption energies and the diffusion barriers all show a bilayer oscillation due to QSE with the unstable (stable) Pb film having a lower (higher) diffusion barrier. The growth morphology of Pb islands on Si(111) can be affected by QSE not only through modification of the energy minima as commonly discussed in the literature, but also clearly through the single atom terrace diffusion barrier oscillation.

[1] A. R. Smith, K.-J. Chao, Q. Niu, and C. K. Shih, Science **273**, 226 (1996).
[2] L. Gavioli *et al.*, Phys. Rev. Lett. **82**, 129 (1999).
[3] K. Budde *et al.*, Phys. Rev. B **61**, R10602 (2000); V. Yeh *et al.*, Phys. Rev. Lett. **85**, 5158 (2000); M. Hupalo *et al.*, Phys. Rev. B **64**, 155307 (2001); M. Hupalo *et al.*, Surf. Sci. **493**, 526 (2001).
[4] Z. Zhang, Q. Niu, and C.-K. Shih, Phys. Rev. Lett. **80**, 5381 (1998).
[5] C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).
[6] W. B. Jian, W. B. Su, C. S. Chang, and T. T. Tsong, Phys. Rev. Lett. **90**, 196603 (2003).
[7] P. Czoschke, H. Hong, L. Basile, and T.-C. Chiang, Phys. Rev. B **72**, 035305 (2005).
[8] I. B. Altfeder, V. Narayanamurti, and D. M. Chen, Phys. Rev. Lett. **88**, 206801 (2002).
[9] H. Brune, Surf. Sci. Rep. **31**, 125 (1998).
[10] J. Tersoff, A. W. Denier van der Gon, and R. M. Tromp, Phys. Rev. Lett. **72**, 266 (1994).
[11] Vienna *ab initio* simulation package, Technische Universität Wien, 1999; G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); G. Kresse and J. Furthmuller, *ibid.* **54**, 11 169 (1996).
[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
[13] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).
[14] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991).
[15] H. J. Monkhorst and J. D. James, Phys. Rev. B **13**, 5188 (1976).
[16] It is reasonable to assume that for the islands of unstable heights, the local energy minima close to the edge of the island top are lower in energy than those close to the center since the Pb atoms are observed experimentally to nucleate at the edge.
[17] P. Politi and C. Castellano, Phys. Rev. E **66**, 031605 (2002).
[18] J. Rottler and P. Maass, Phys. Rev. Lett. **83**, 3490 (1999).
[19] J. Krug, P. Politi, and T. Michely, Phys. Rev. B **61**, 14 037 (2000); S. Heinrichs, J. Rottler, and P. Maass, Phys. Rev. B **62**, 8338 (2000).