PHYSICAL REVIEW B **78**, 193407 (2008)

Height-dependent nucleation and ideal layer by layer growth in Pb/Pb(111)/Si(111)

S. M. Binz, M. Hupalo, and M. C. Tringides*

Department of Physics and Ames Laboratory, USDOE, Iowa Sate University, Ames, Iowa 50011–9557, USA

(Received 14 July 2008; revised manuscript received 3 October 2008; published 26 November 2008)

It has been puzzling why for Pb/Si(111), oscillations have been observed at temperatures as low as 18 K and were found to improve with decreasing temperature. With scanning tunneling microscope we have directly observed this ideal layer by layer growth. A dramatic dependence of the second layer island morphology on island height, expected from quantum size effects (QSE), is also found. Low density of fractal islands on stable vs high density on unstable Pb islands on a mixed height island confirms the role of QSE in kinetics. The low diffusion barrier and the fractal island morphology can explain the unusual layer by layer growth.

DOI: 10.1103/PhysRevB.78.193407 PACS number(s): 61.05.jh, 68.35.Ct, 68.37.Ef, 68.55.J−

Epitaxial growth has been of interest over the last three decades because novel types of nanostructures can be fabricated in controlled ways. Depending on the system, either layer by layer growth (i.e., a layer is completed before the next one nucleates on top) or three-dimensional growth is observed (when many layers are occupied simultaneously). Layer by layer growth is commonly observed at sufficiently high temperatures so diffusion of the deposited atoms is fast, and hopping from higher to lower layer occurs prior to the onset of nucleation.

A widely used experimental method to monitor *in situ* the quality of a grown film is diffraction intensity oscillations.[1–4] Strong sustained oscillations are evidence that the film is growing smoothly, while monotonically decaying oscillations are evidence of three-dimensional growth. However, it was puzzling when sustained oscillations were observed well below room temperature because they imply a very low diffusion barrier, unless some nonthermal diffusion mechanism is operating; one possibility is transient mobility[5] related to the condensation energy that should be dissipated (i.e., to phonons or to electron-hole pairs, etc.) before an atom is eventually adsorbed on the surface. A different mechanism predominantly relevant for metal surfaces is downward "funneling."[6] If a cluster with the minimum number of atoms needed to form a stable binding site has not nucleated, the atom can "funnel" to the lower level.

Low-temperature oscillations have been seen during the growth of Pb/Si(111).[1,2] It became especially puzzling because the oscillation amplitude was larger as the temperature was reduced with the highest quality oscillations observed at the lowest temperature (18 K). Since neither of the two nonthermal mechanisms predicts this inverse dependence on temperature, these intriguing results have not been explained yet.

In addition, Pb growth has been of interest in quantum size effect (QSE)-driven growth observed with numerous techniques[7–12] and has resulted in an unusual degree of self-organization. Sharp uniform height island distributions have been observed [i.e., odd heights when measured from the wetting layer on the Si(111)-7$\times$7]. Height selection can be explained from the variation of the confined electron energy with height, since for stable height islands the highest occupied band (HOB) is further away from the Fermi level than for unstable islands.[8] It is expected that this variation can also affect island reactivity by modifying the barriers of the atomistic processes controlling reactivity (adsorption, diffusion, nucleation, and bonding). It has been an active question to find how these barriers are modified with island height for stable and unstable heights.[13–16]

In this Brief Report scanning tunneling microscope (STM) experiments were performed on the growth of Pb/Pb(111) at 40 K [with the initial substrate Pb islands grown on Si(111)-(7$\times$7)] and almost perfect layer completion (within 95%) is observed, before the next one starts to nucleate, which is in agreement with the strong low-temperature diffraction oscillations. This is partially attributed to the very low diffusion barrier of Pb on Pb(111) (less than 80 meV). Furthermore, the second layer nucleation shows dramatically different morphology where growth on a stable height results in low-density fractal-like islands, but growth on an unstable height results in high density of smaller islands. These differences can be attributed to the variation of the electronic structure of the island with height. Remarkably, this difference in morphology is observed on a single mixed island grown over a substrate step; the stable five-layer part of the island has 60 times lower island density than the unstable four-layer part, indicating that the QSE stability condition normal to the surface is completely decoupled from the lateral degrees of freedom of the confined electrons. The low diffusion barrier and the fractal island morphology can account for the improved oscillations as the temperature is lowered.

If Pb islands are grown initially at 240 K, a wider range of heights can form (four, five, six, and seven layers) because at this higher temperature the islands reach large lateral sizes (they exceed 150 nm) which enhances island stability over longer times both for unstable and stable heights.[17] The unstable islands will eventually grow into stable islands but over the course of hours. An amount of 1.35 ML of Pb was deposited at 240 K on Si(111)7$\times$7 followed by cooling the sample to 40 K. Small amounts of Pb were deposited at 40 K with flux rate of 0.4 ML/min. A five-layer island was selected to observe how the second layer grows with Pb deposition.

Experiments were also carried out by depositing Pb directly on the Si(7$\times$7) at 40 K (without first growing large islands at 240 K). Initially, an amorphous layer of Pb is observed which transforms to a crystalline layer at ~4 ML.[1,2] Although it is easier to observe this crystallographic transition with diffraction, it is also seen with STM. A change in

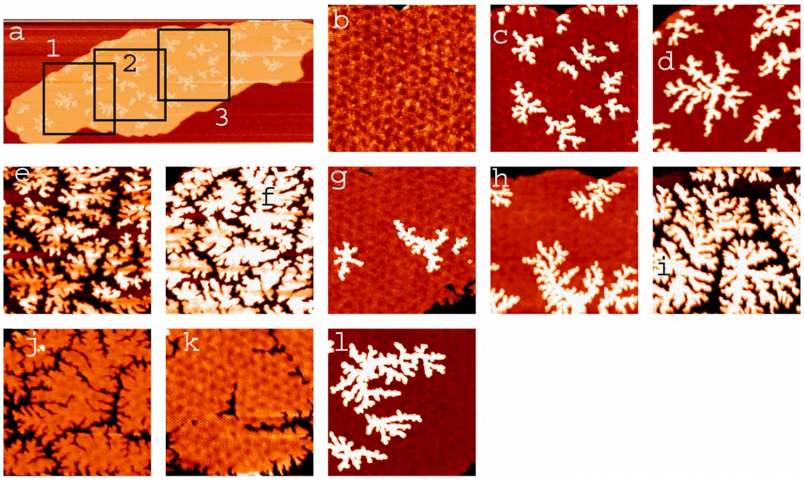

FIG. 1. (Color online) Stepwise deposition experiments at 40 K with flux rate of 0.4 ML/min on top of a large five-layer island which is pregrown at 240 K. All images are 100×100 nm^2 and are outlined as the black squares in (a) [except (a) which is 403×162 nm^2 and (d) which is 73.45×73.45 nm^2]. Images (b)–(l) are all close up images of the outlined parts in (a). The sequence of images shows how the growth is perfect layer by layer. The amount added above the initial growth at 240 K, $\Delta\theta$, in each image is (a) 0.1, (b) 0.0, (c) 0.1, (d) 0.2, (e) 0.4, (f) 0.6, (g) 1.0, (h) 1.2, (i) 1.4, (j) 1.6, (k) 1.8, and (l) 2.0 ML.

the grown morphology from a granular structure with well-separated random features is first observed, but after crystallization flat interconnected regions span the whole image. Only two layers are exposed at the growing front at all coverages, which confirms the layer by layer growth as in the diffraction experiments. However, results on isolated five-layer island grown at 240 K are shown because it is easier to monitor the coverage (from the uncovered regions on the island) and to assess how ideal the layer by layer growth is.

Figure 1 shows the five-layer island evolution with increasing Pb coverage. In Fig. 1(a) a full view of the five-layer island is shown over an area of 403×162 nm^2. The other images [Figs. 1(b)–1(l)] show successive images after depositing small Pb amounts listed in the figure caption. The scale is 100×100 nm^2, which is outlined in Fig. 1(a) [except for Fig. 1(d) which has 73.45×73.45 nm^2]. Figure 1(b) shows that on the flat clean surface, a periodic pattern of spatial period (8.3 nm) forms with an amplitude of less than 0.03 nm. Most likely this is an electronic effect that is a result of beating between the two different lattices at the Pb-Si interface. The period corresponds approximately to three times the 7×7 unit cell and is aligned with the $[1\bar{1}0]$ directions. This pattern is observed both on the five- and four-layer islands with the same contrast (the compact "blobs" are dark and the surrounding "sea" is bright), which shows that the island has perfect *ABC* stacking as dictated by the bulk structure underneath (of the Pb island). Islands grown with different stacking (*ABC* or *ACB*) result in reversal of the corrugation contrast after each monolayer increment.[18,19] Depending on the specific metal system the correct stacking is followed [Ag/Ag(111)],[20] but in other systems with stacking faults are also seen [Ir/Ir(111)].[21]

As will be discussed further below, the islands formed on the five-layer island have fractal shapes and lower density than the ones formed on the four-layer island. The island density at 40 K is higher by a factor of ~60 than the island density on the five-layer island. With further Pb deposition, the fractal islands develop more branches (and the arm width is approximately constant 2.5 nm) until eventually they fill in the layer. It is instructive to focus on the completion of the sixth layer [in Fig. 1(g) by adding 0.4 ML to the previous image for a total of 1 ML] and the completion of the seventh layer [in Fig. 1(l) by adding 0.2 ML for a total of 2 ML]. In both cases, the growing layer is completed perfectly before islands nucleate in the next layer and all the "cracks" are healed. This is consistent with a large diffusion length. When the separation between cracks becomes comparable to the distance between the first nucleated islands [seen in Fig. 1(c)], coexistence between remaining "cracks" and newly nucleated islands is possible. However, the fractal morphology suppresses nucleation close to the "cracks" and induces their filling. The last part of the five-layer island to be completed is the outside edge of the five-layer island (not shown) for some still not understood reason. The layer by layer growth independently confirms that the Pb follows the *ABC* stacking; otherwise "cracks" would remain since regions of different stacking coming in contact would never heal.

The difference in the grown morphology depending on island stability is seen in a very intriguing way in Fig. 2. The island shown was also prepared at 240 K, but because it extends over a substrate step the left part is five layers and the right part is four layers. After cooling down to 40 K and depositing 0.23 ML, the second layer nucleation morphology is very different on the two parts; they are acting independently as if they were not connected, i.e., the five-layer part has a few fractal islands while the four-layer part has a larger number of smaller compact islands. Integrating the coverage on the two parts (and correcting the expected larger contribution of tip convolution for the smaller islands) results in the same coverage for the two parts. The nucleation on the two parts suggests the presence of a large reflecting barrier on the island top running along the buried step underneath. Diffusion on top of each part is restricted, forcing the deposited atoms to remain within each part (although the difference in height between the two parts is only 0.02 nm). Despite this initial difference of the second layer nucleation on the two parts, both layers are completed at the same time. Comparison of island densities and coverage on each part of the mixed island and separate islands of the same height support fully the conclusions that the coverage on each part is the amount fallen on each top and diffusion between the two parts is restricted.

One can draw several conclusions from this experiment. First, there is likely a barrier on the island top related to QSE effects. This is a direct evidence that QSEs affect kinetic

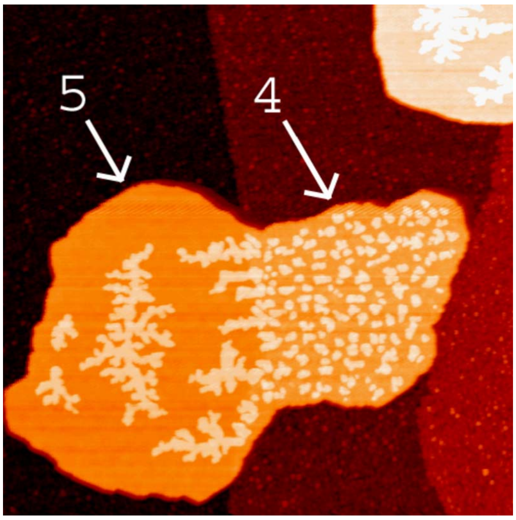

FIG. 2. (Color online) $200\times 200\ \text{nm}^2$. An island that spans a single-step edge with 0.23 ML of Pb deposited at 0.1 ML/min. The left part of the island is five and the right part is four layers high. The island is flat with a 0.075 nm height difference between the two parts. The four-layer part has higher density of small compact islands while the five-layer part has lower density of bigger fractal islands because of QSE. The coverage is the same in the two parts so the two island parts behave as if they are not connected.

barriers and nucleation, and that reactivity changes can be dramatic (although the present system is a homoepitaxial system). The larger variation observed in the current experiment (the factor of ~60 difference in island density) may also be related to the smaller island heights (four-layer vs five-layer) since QSE differences are larger at lower heights.

How can the dramatic difference in the observed morphology between the two island parts be explained? In Ref. 15 Fe deposition experiments on large Pb islands of heights 12–17 ML at 150 K have shown an island density variation with height of at most a factor of 1.3, which was attributed to the terrace diffusion barrier being lower by $E_4-E_5\approx -0.017$ eV on the unstable (E_4) vs stable (E_5) height island and the same critical size cluster $i=1$ on both heights. (The critical size cluster is the minimum island size above which the island does not decay.) The current experiments suggest that at 40 K the origin of the different morphology is the difference in the critical size cluster and not of the terrace diffusion as in Ref. 15. Assuming $i=1$ as in Ref. 15 results in $E_4-E_5=0.04$ eV with the positive difference inconsistent with previous work, i.e., how QSE affect terrace diffusion.[15,22] The island density difference in Fig. 2 implies that the critical size cluster i is larger on the five than on the four-layer island. This should be expected since four-layer islands are unstable. The nucleation of even small monolayer islands on top of the four-layer island lowers their energy, since these new islands add Pb to create a stable height. On the other hand, nucleation on the top of five-layer islands, which are stable, increases their energy because it adds atoms to create an unstable height, so it requires the aggregation of many more atoms in irregular fractal-like shapes. Edge diffusion must be extremely low at 40 K which can account for the fractal morphology; this is not surprising because it has been seen in other metal systems.[20,21,23]

To obtain a more quantitative estimate of possible values of the critical size cluster and terrace diffusion barriers on the two parts, the scaling theory of nucleation is employed as a first way to estimate the differences. Analyzing the four-layer island density under the simplest assumption that $i=1$

$$n=\eta(D/F)^{-1/3} \tag{1}$$

and using $D=1\times 10^{13}\exp(-E_4/kT)$, where $\eta\approx 0.25$ is a numerical prefactor, $n=0.03\ \text{islands/nm}^2$ is the measured island density, the flux rate is $F=1.66\times 10^{-3}\ \text{ML/s}$, $T=40$ K, the Pb(111) density is $9.41\ \text{unit cells/nm}^2$, we get $D=828$ hops/s or the four-layer barrier $E_4=0.08$ eV.

For the five-layer island we expect $i\gg 1$.[24] Based on the scaling theory of nucleation

$$D=F(n/\eta)^{-(i+2/i)}\{[\exp(E_i/(i+2)kT)/n]^{i+2/i}\} \tag{2}$$

with all the symbols defined earlier except the cohesive energy E_i. For fixed F, T, and sufficiently low E_i increasing i increases the diffusion activation energy. Since it is known[15,22] that the diffusion barrier for unstable islands E_5 must be lower than the barrier for stable islands E_4, for the measured island densities to have a difference in barriers $E_5-E_4>0.01$ eV requires a minimum value of $i=10$ and a maximum value of $E_i=0.1$ eV. Increasing E_i makes the difference E_5-E_4 smaller. This change in critical size cluster from 1 to 10 as a function of height is very dramatic, proving that QSE can be another controlling factor of the observed morphology. The terrace diffusion barriers (0.08 and 0.09 eV) are slightly higher than the barriers for stable height islands calculated by first principles in Ref. 22 to fit the nucleation data at higher temperature 180–210 K. At higher temperatures, other processes become important (i.e., transfer between the island top to the wetting layer, hopping from the top to the wetting layer, etc.). These barriers are "frozen" out at 40 K in the current experiments which allows a more direct way to extract the controlling factor, which is the critical size cluster i.

In summary the ideal layer by layer growth, the low diffusion barriers, and the fractal-like island morphology can account for the enhancement of the diffraction oscillations at these low temperatures that have been puzzling so far. In addition the current experiments present strong evidence that geometry can control the electronic structure, adatom adsorption, nucleation, and possibly reactivity of the grown islands because of QSE. It is also remarkable that the presence of the step below completely separates the two parts of the mixed island so that they behave independently. This shows that the quantization along the normal direction of the confined electrons is separable and not coupled to the lateral degrees of freedom.

Work at Ames Laboratory was supported by the Basic Sciences, U.S. Department of Energy under Contract No. DE-AC02_07CH11358.

*Corresponding author. FAX: 515 294 0689.
tringides@ameslab.gov

[1] M. Jałochowski, M. Hoffmann, and E. Bauer, Phys. Rev. B **51**, 7231 (1995).

[2] A. Petkova, J. Wollschläger, H.-L. Günter, and M. Henzler, Surf. Sci. **482-485**, 922 (2001).

[3] P. B. Howes, K. A. Edwards, D. J. Hughes, J. E. Macdonald, T. Hibma, T. Bootsma, and M. A. James, Surf. Sci. **331-333**, 646 (1995); K. A. Edwards, P. B. Howes, J. E. Macdonald, T. Hibma, T. Bootsma, and M. A. James, *ibid.* **424**, 169 (1999).

[4] M. C. Tringides, in *Morphological Organizations in Epitaxial Growth and Renewal*, edited by Z. Zhang and M. G. Lagally (World Scientific, Singapore, 1998).

[5] W. F. Egelhoff, Jr. and I. Jacob, Phys. Rev. Lett. **62**, 921 (1989).

[6] J. W. Evans, D. E. Sanders, P. A. Thiel, and Andrew E. DePristo, Phys. Rev. B **41**, 5410 (1990).

[7] K. Budde, E. Abram, V. Yeh, and M. C. Tringides, Phys. Rev. B **61**, R10602 (2000).

[8] M. Hupalo and M. C. Tringides, Phys. Rev. B **65**, 115406 (2002).

[9] W. B. Su, S. H. Chang, W. B. Jian, C. S. Chang, L. J. Chen, and T. T. Tsong, Phys. Rev. Lett. **86**, 5116 (2001).

[10] A. Mans, J. H. Dil, A. R. H. F. Ettema, and H. H. Weitering, Phys. Rev. B **66**, 195410 (2002).

[11] M. H. Upton, C. M. Wei, M. Y. Chou, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **93**, 026802 (2004).

[12] C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).

[13] L. Aballe, A. Barinov, A. Locatelli, S. Heun, and M. Kiskinova, Phys. Rev. Lett. **93**, 196103 (2004).

[14] A. G. Danese, F. G. Curti, and R. A. Bartynski, Phys. Rev. B **70**, 165420 (2004).

[15] Xucun Ma, Peng Jiang, Yun Qi, Jinfeng Jia, Yu Yang, Wenhui Duan, Wei-Xue Li, Xinhe Bao, S. B. Zhang, and Qi-Kun Xue, Proc. Natl. Acad. Sci. U.S.A. **104**, 9204 (2007); L.-Y. Ma, L. Tang, Z.-L. Guan, K. He, K. An, X.-C. Ma, J.-F. Jia, Q.-K. Xue, Y. Han, S. Huang, and F. Liu, Phys. Rev. Lett. **97**, 266102 (2006).

[16] N. Binggeli and M. Altarelli, Phys. Rev. Lett. **96**, 036805 (2006).

[17] M. Hupalo and M. C. Tringides, Phys. Rev. B **75**, 235443 (2007); Z. Kuntova, M. Hupalo, Z. Chvoj, and M. C. Tringides, *ibid.* **75**, 205436 (2007).

[18] W. B. Jian, W. B. Su, C. S. Chang, and T. T. Tsong, Phys. Rev. Lett. **90**, 196603 (2003).

[19] T. L. Chan, C. Z. Wang, M. Hupalo, M. C. Tringides, W. C. Lu, and K. M. Ho, Surf. Sci. Lett. **600**, 179 (2006).

[20] E. Cox, M. Li, P. W. Chung, C. Ghosh, T. S. Rahman, C. J. Jenks, J. W. Evans, and P. A. Thiel, Phys. Rev. B **71**, 115414 (2005).

[21] C. Busse and T. Michely, Surf. Sci. **552**, 281 (2004).

[22] T.-L. Chan, C. Z. Wang, M. Hupalo, M. C. Tringides, and K. M. Ho, Phys. Rev. Lett. **96**, 226102 (2006).

[23] H. Röder, K. Bromann, H. Brune, and K. Kern, Phys. Rev. Lett. **74**, 3217 (1995).

[24] J. G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995).