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# Kinetics measurements of Pb island growth on Si(111)

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We present the results of kinetics experiments on quantum-size-effects (QSE) Pb islands formed on Si(111). We have looked at the evolution of seven-layer Pb islands from five-layer Pb islands due to the transport of Pb atoms from the interisland region, overcoming a barrier at the island edges, and moving to the island tops. By analyzing low-energy electron-diffraction and scanning-tunneling microscopy data, we have estimated the barrier for layer formation in this system to be ~0.32 eV. This energy is much larger than that expected from QSE electronic contributions alone.

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## I. INTRODUCTION

Nanoscale structures and films are now being routinely produced in laboratories.[1–6] One of the important findings in this research is that the size of these nanostructures is related to their electronic structure.[6,4,3] That is, the confinement of the electron wave function for small objects leads to sharp energy levels, implying a strong dependence of the total energy of the confined electrons on the nanoobject's size or shape. This relation is referred to as quantum size effects (QSE).[1] A consequence of this relationship is that certain film thicknesses or certain island heights are more stable than others.[7] One such system is the growth of Pb islands on Si(111).[4] It has been shown that the Pb islands grow as straight-sided columns with a very narrow height distribution on top of a Pb wetting layer above the Si(111) surface. Depending on growth conditions, the maximum in the island-height distribution can be changed but is always found to be peaked in increments of two Pb layers. The reason for the bilayer stability is partially understood in terms of energy oscillations in the electronic energy $E(h)$ as a function of their height $h$.[8] The oscillations occur as quantum well states pass below the Fermi energy leading to minima in the electronic energy of particular island heights.[8,9]

Studies of the QSE system Ag/GaAs(110) have attempted to measure the difference in the electronic energy minima between ''magic'' thicknesses assuming that the height evolution is controlled solely by depth of the potential minima in $E(h)$.[6] In other words it is assumed that the island-height distribution has a purely thermodynamic origin. However, such an analysis does not take into account all the relevant information about the island buildup. Even though the minima in $E(h)$ are useful for stability comparison, the saddle-point maxima in the potential-energy surface separating the minima of the different island heights are equally important in determining which heights are observed. As we will show, kinetic barriers can be as large as or larger than the differences in the electronic energy minima. So while QSE offers thermodynamic reasons for the formation of preferred height islands, it does not provide an answer regarding how a given height will be selected at a given temperature, nor does it predict the time necessary for an island's growth to be completed. In other words the preferred island-height distribution is a result of the energy gain because of QSE, only as long as atoms can hop over the controlling kinetic barriers.

In the case of QSE islands on the system Pb/Si(111), the reason for the observed narrow island-height distributions is far from resolved. Thermodynamically, one could argue that the Gibb's phase rule could select out one or two stable island sizes. While it is known that islands of seven layers are of the lowest in energy and preferred for Pb coverages of $\Theta < 7$ ML, they only forms if the system is heated above 180 K.[10] Furthermore, the island-height distribution is not reversible with temperatures. Both of these observations suggest kinetic limitations to the island sizes. Even if the island-height distribution had a thermodynamic origin, one would want to know why islands instead of ordered two-dimensional films are seen experimentally. What is the source of the rate-limiting barrier that leads to the observed island heights and shape distribution? Is it diffusion between islands, diffusion up the island sides, or a step-edge barrier at the island perimeter? It is the answers to these questions that are the motivation for the work presented here.

In this paper we present an investigation into the kinetics of the way in which QSE Pb islands grow on Si(111). In particular we examine how five-layer-height Pb islands transform into seven-layer islands at fixed temperature by changing the Pb coverage. We have constructed an experiment in which a known amount of material, separate from the Pb in the wetting layer, is used to build seven-layer islands from five-layer islands. The results of these experiments allow us to conclude that the rate-limiting barrier to island formation at $T \sim 180$ K is the step-edge barrier for a Pb atom to move to the top of the five-layer islands. We estimate this barrier to be $0.32 \pm 0.05$ eV. The estimated barrier energy is larger than the difference between five- and six-layer island electronic energies alone.

## II. EXPERIMENTAL TECHNIQUE

All of the experiments were carried out in an ultrahigh vacuum (UHV) system ($p = 2 \times 10^{-11}$ torr) using a commercial spot profile analysis low-energy electron-diffraction

(LEED) system.[11] All the momentum transfers, $\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$, are reported as $q_\parallel$ and $q_\perp$, parallel and perpendicular to the Si(111) plane, respectively. $q_\parallel$ points along the $[1\bar{1}0]$ direction and is normalized to the Brillouin zone of Si(111), $q_\parallel^* = q_\parallel/(2\pi/a)$, $a=3.84$ Å, while $q_\perp$ is normalized to the Pb (111) interlayer spacing, $q_\perp^* = q_\perp/(2\pi/d)$, $d=2.86$ Å. The scanning-tunneling microscope (STM) experiments were carried out in a separate UHV system using a commercial Omicron STM as described elsewhere.[10] The silicon sample was cleaned using standard techniques.[12] Pb was deposited using a fully outgassed Knudsen cell source monitored by a quartz thickness monitor. The coverage was calibrated (both at low and room temperatures) using the break in the Si-Auger line versus Pb deposition time (as described in Ref. 13). In all the experiments reported here the Pb flux was constant: $\sim 1$ ML/min ($1\ \text{ML}=7.84\times 10^{-2}$ atoms/Å$^2$).

The basic experiment we report is the investigation of the kinetics of Pb island growth. There are three possible rate-limiting processes that must be considered: (i) the barrier to single Pb-atom diffusion on the wetting layer, (ii) the barrier to single Pb-atom diffusion on the facet planes of the island sides, and (iii) the barrier for diffusion at the island edges. As we will show by direct observation in Sec. III, both the wetting layer and the island facet diffusion barriers are much smaller than the barrier at the island edges. Therefore, the experiments outlined below are designed to measure the kinetics of Pb atoms moving over the island edges.

The experiment begins by first preparing a known island-height distribution at a growth temperature, $T_G$. This is done by depositing 4 ML of Pb on the Si(111) substrate at 130 K and then annealing the film at $T_G$ for 10 min to form the islands. A particular height distribution can be chosen by properly selecting $T_G$. In the experiments discussed here, we are interested in the growth of seven-layer-height islands from five-layer-height islands. From previous experiments we know that by changing $T_G$ from 150 K to 180 K the island-height distribution can be altered from predominately five-layer islands at 150 K to predominately seven-layer islands at 180 K.[10] Both island radius, *R*, and island separation, *S*, were also measured for each growth temperature. The island diameter is determined by measuring the full width or half maximum of the Pb (10) LEED spot, while the island spacing is determined from measurements of the satellite peak positions (Henzler rings) around the (00) specular beam.[14] For the temperature range used in these experiments, the island diameters range from 90 Å for five-layer islands at 160 K to 125 Å for seven-layer islands at 180 K. The island spacing is $\approx 400$ Å for both five- and seven-layer islands in this temperature range.

The island distributions formed at each growth temperature and total Pb coverage, $\Theta$, are measured while cooling the sample to 130 K. For each $T_G$ we measure the relative area per Si $(1\times 1)$ unit cell of five- and seven-layer islands as well as the area of the wetting layer; denoted by $A_5$, $A_7$, and $A_W$, respectively (see Fig. 1).

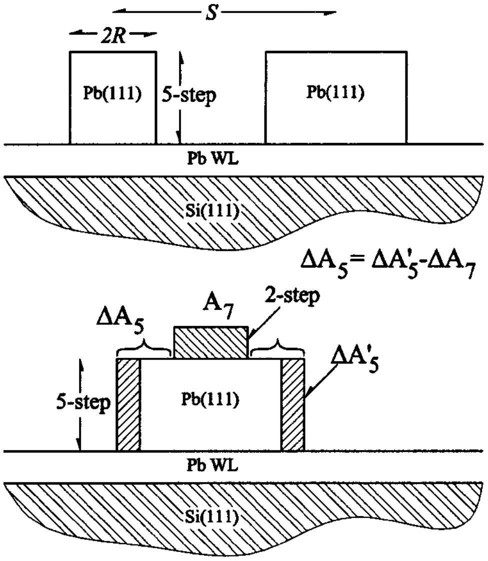

FIG. 1. Schematic of the growth of five-layer to seven-layer islands showing definitions of the pertinent measured quantities.

Once a particular island distribution is grown and measured, an additional 0.5 ML of Pb is deposited at $T_G$. The change in the relative area of the five- and seven-layer islands due to this additional Pb is then determined. The experiment is repeated for several temperatures in the range $160\ \text{K} < T_G < 180\ \text{K}$. Therefore, at each $T_G$, we monitor how the additional Pb is incorporated into different height islands. As is shown in Sec. IV, the temperature dependence of the change in the island area is related to the barrier for atoms moving from the interisland area to the island tops.

We point out that the kinetics experiments described above are carried out as a function of coverage at constant temperature. We know from previous experiments that atoms move to the islands when the system is heated from a lower to a higher growth temperature.[10] Since the additional 0.5 ML is deposited at the same $T_G$ as the initial deposition, we can be confident that all the mass transfer from the wetting layer to the islands has already been completed during the initial deposition. This is important, since it allows us to conclude that all the changes in the island height or island size from the initial distribution are only related to the 0.5 ML of Pb added and not from Pb atoms still residing in the wetting layer or in the islands themselves.

## III. RESULTS

The island-height distributions before and after the additional Pb deposition were measured from the $q_\perp$ dependence of the LEED specular (00) peak profiles between two in-phase diffraction conditions (an in-phase diffraction point occurs when $q_\perp^* = \text{integer}$). Details about this procedure can be found in Refs. 4,11,15, and 16. To summarize, at each $q_\perp^*$ the peak profile is fit to a two-component line shape. The broad component (area $a_I$) is used to represent the Henzler rings produced by the islands.[14] The narrow component (area $a_S$) reproduces the diffraction from the exposed surface.[15,16] An example of such a fit is shown in Fig. 2. The ratio of these areas is used to generate the function $g(q_\perp^*) = 1/(1 + a_I/a_S)$. Information on the island-height distribution comes from the fact that diffraction interference between the

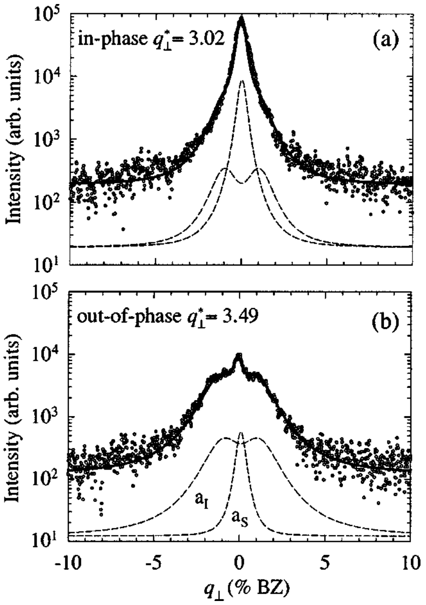

FIG. 2. Two-component fits to the (00) specular beam for $\Theta = 4$ ML and $T_G = 170$ K. (a) An in-phase condition $q_\perp^* = 3.02$. (b) An out-of-phase condition $q_\perp^* = 3.49$. Circles are data; solid line is best fit. Dashed lines are the decomposed narrow and broad components with integrated areas $a_S$ and $a_I$, respectively.

top of the islands and the region between the islands gives rise to oscillations in $g(q_\perp^*)$. The function $g(q_\perp^*)$ will oscillate between two in-phase conditions with a periodicity proportional to the island height (i.e, $n$ oscillations for islands of height $n$). An example of the oscillations in $g(q_\perp^*)$ for seven-layer islands is shown in Fig. 3.

The exact shape of $g(q_\perp^*)$ versus $q_\perp^*$ depends on the relative amounts of five- and seven-layer islands present relative to the wetting layer. Therefore, to extract $A_5$, $A_7$, and $A_W$ from the $g(q_\perp^*)$ data, we compare the experimental data to $g(q_\perp^*)$ calculated from an assumed distribution of $A_i'$'s. To do this we write $g(q_\perp^*)$ within the kinematic model,[4]

$$g(q_\perp^*) = |A_W + A_5 e^{i2\pi q_\perp^* 5} + A_7 e^{i2\pi q_\perp^* 7}|^2, \tag{1}$$

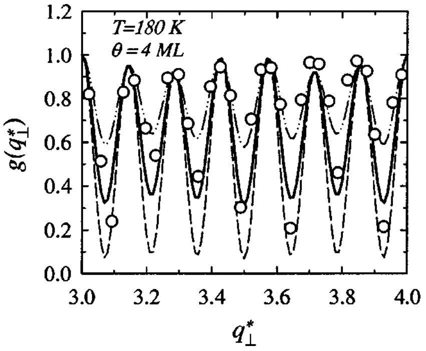

FIG. 3. $g(q_\perp^*)$ vs $q_\perp^*$. The data (○) is from a distribution of predominately seven-layer Pb islands grown at 180 K and $\Theta = 4$ ML. The best fit (solid line), as described in the text, is for $A_7 = 0.20$ and $A_5 = 0.02$. For comparison two poorer fits are shown using $A_7 = 0.10$ and $A_5 = 0.02$ (dash-dotted line) and $A_7 = 0.30$ and $A_5 = 0.02$ (dashed line).

where the areas are subject to the constraint equation

$$\sum_n A_n = 1. \tag{2}$$

We have looked extensively for evidence of six-layer islands in these fits and find no indication of any significant concentration. Similarly, STM images show no evidence for six-layer islands. Therefore, we have confidently left out a term $A_6$ for six-layer islands in the fitting routine.

In principle, only $A_5$ and $A_7$ are adjustable parameters because of the constraint, Eq. (2), forcing $A_W$ to vary accordingly. From the total amount of Pb deposited and the extracted area $A_W$ from the fits, the Pb wetting-layer thickness can be found. In effect this means that the amount of Pb in the wetting layer is treated as an adjustable parameter. In principle, the wetting-layer thickness contributes to the measured $g(q_\perp^*)$ but we do not explicitly include it in Eq. (1). Instead we have chosen to allow $A_W$ to be an adjustable parameter in the fits. There are two justifications for this. First, the scattering amplitudes, $f_i'$'s, from each layer are assumed to be equal and have been set to 1.0 in Eq. (1). Since the amplitude in a $g(q_\perp^*)$ curve is a function of both the $A_i'$'s and the corresponding scattering factors at each layer, it is clear that either increasing $f$ or the occupation of the layer will have a qualitatively similar effect on the oscillation amplitude. In another publication we show that, with mild annealing from 120 K to 180 K, Pb is transferred from the wetting layer to the islands with a corresponding increase of $f_W$.[17] Since the two effects (i.e., transfer of Pb to the islands and an increase in $f_W$) provide opposite contributions to the amplitude of the $g(q_\perp^*)$ curve, the use of $A_W$ as an adjustable parameter is justified. Second, we are interested in extracting the relative changes $\Delta A_5$ and $\Delta A_7$ that are determined by the difference in the amplitude of the $g(q_\perp^*)$ curves for 4 ML and 4.5 ML, where $A_W$ is presumably the same. This means that the amplitude differences and the corresponding changes to the layer occupation $\Delta A_5$ and $\Delta A_7$ are not very sensitive to $A_W$.

A $\chi^2$ fitting routine is used to match the calculated $g(q_\perp^*)$ to the measured value. Examples of fits for different choices of $A_7$ are shown in Fig. 3 for a temperature at which predominately seven-layer islands exist, $T_G = 180$ K. As can be seen the oscillation amplitude is very sensitive to $A_7$. In order to establish error bars we also looked at fits that calculated $\chi^2$ based on the minima points alone in the $g(q_\perp^*)$ curves. This procedure gave areal coverages $\sim 0.04$ lower than the full fits. However, $\Delta A$ measured using just the minima gave nearly identical values as those derived from the full fits. A detailed analysis of the fitting routine shows that changes in the areal concentrations, $\Delta A_5$ and $\Delta A_7$, are accurate to within $\pm 0.02$.

Once the island-height distribution, mean island size, and mean separation are measured, the system was heated back to its original growth temperature where an additional 0.5 ML of Pb was deposited at the same flux rate of 1 ML/min. The island-height analysis described above was then repeated. Figure 4 shows a comparison between $g(q_\perp^*)$ curves

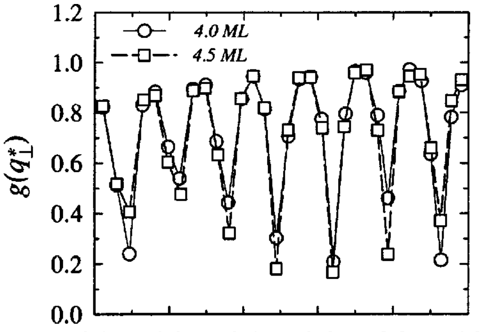

FIG. 4. A comparison of experimental $g(q_\perp^*)$ vs $q_\perp^*$ for $T_G = 180$ K for two different coverages. Circles on the solid line represent data for $\Theta = 4.0$ ML ($A_7 = 0.20$ and $A_5 = 0.02$). Squares on the dashed lines represent data for $\Theta = 4.5$ ML ($A_7 = 0.26$ and $A_5 = 0.02$).

for coverages of 4.0 ML and 4.5 ML at $T_G = 180$ K. The amplitude difference between the two curves is due to the change in the layer occupancy. These differences in $g(q_\perp^*)$ before and after deposition are uniquely determined by $\Delta A_5$ and $\Delta A_7$. For the temperature in Fig. 4 the amplitude increase is due to an increase in $A_7$. Similar curves for each temperature were analyzed. The results of these experiments are summarized in Fig. 5.

## IV. DISCUSSION

We can identify three temperature regimes in Fig. 5: (i) for $T \leqslant 155$ K the surface is initially covered by five-layer islands and subsequent Pb deposition leads to an increase in five-layer islands; (ii) for $155 \text{ K} < T < 175$ K a mixture of five- and seven-layer islands is present in the initial distribution. Subsequent Pb deposition leads to an increase in seven-layer islands and a decrease in five-layer islands; (iii) above 175 K the initial surface primarily consists of seven-layer islands, with subsequent Pb deposition increasing the seven-layer island area. For this work, we will focus on understanding the structural evolution of Pb islands in regions (ii) and (iii).

In region (iii), above 175 K, few five-layer islands exist in the initial distribution. Practically all the additional 0.5 ML of material in the second deposition moves to the seven-layer islands. This statement is first supported by the fact that $\Delta A_7$ at 180 K is close to the maximum increase obtainable for 0.5-ML additional Pb coverage (assuming no five-layer islands), 7%, ($\Delta A_7^{\max} = 0.5 \text{ ML}/7 = 0.07$). Secondly, measurements of the island sizes and island separation after deposition show no increase in the number of seven-layer islands above 175 K. Finally, STM experiments show that none of the additional 0.5 ML is seen in the region between islands at this temperature. These observations suggest that in the temperature range $175 \text{ K} < T < 180$ K all of the additional Pb deposited is added to existing seven-layer islands. Since the initial seven-layer island coverage is less than 25%, most of this increase in seven-layer island area must be due to additional Pb landing between islands and diffusing to the sides of existing seven-layer islands up to five-layers ($\sim 0.35 \text{ ML} = 5\Delta A_7^{\max}$), followed by the remaining 0.15 ML diffusing to the island tops to form the sixth and seventh layers.

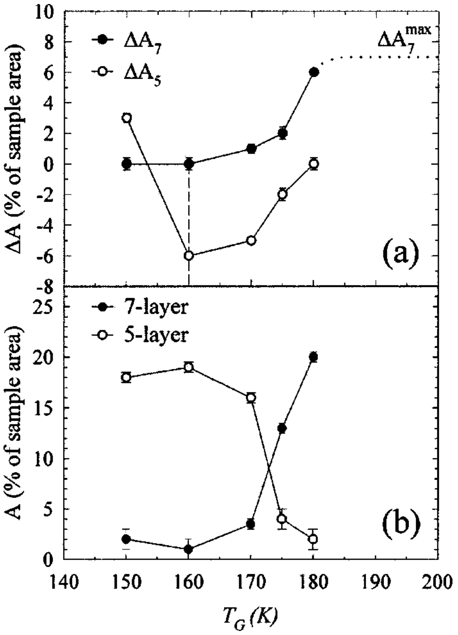

FIG. 5. (a) Change in island area vs. $T_G$ of 5- (○) and 7-layer islands (●) after depositing an additional 0.5 ML of Pb. Dotted line shows the saturation value $\Delta A_7^{\max}$. Vertical dashed line marks the onset of seven-layer island nucleation. (b) Island area vs. $T_G$ of 5- (○) and 7-layer islands (●) from the initial Pb deposition.

These observations lead us to one of the central findings of these experiments: the controlling barrier that must be overcome to grow the sixth and seventh layers above 175 K is the one related to moving the Pb to the last two layers. This statement is supported by a number of other observations. First, at $T > 175$ K, the system is well above the temperatures favoring the completion of predominantly five-layer islands ($T \sim 150$ K). This implies that the barrier to forming five-layer columns at the sides of existing seven-layer islands is small relative to $kT$ in regime (iii). Second, the lack of any Pb in the interisland region (as determined by STM) along with the fact that all of the additional Pb deposited above 175 K is incorporated into the sides of existing seven-layer islands within the deposition time implies that the mobility of the Pb between the islands is relatively fast. If diffusion on the wetting layer was the rate- limiting step, mild annealing would cause the area of preferred seven-layer islands to increase gradually as more atoms diffuse to the islands so that seven-layer islands would be observed at all temperatures below $\sim 180$ K, with their density decreasing monotonically with temperature. Neither of these effects is observed. Instead, in the range of our experiments, we observe a sharp transition from five- to seven-layer islands with growth temperature [see Fig. 5(b)]. Also the outcome of the growth is the same whether we deposit continuously or in stepwise coverage increments, indicating that diffusion on the wetting layer is very fast. Finally, during growth at a constant $\sim 180$ K, the island density does not change with additional Pb coverage [i.e., the satellite rings of the Pb(00) spot, sensitive to the island separation, do not change]. This indicates that the diffusion length on the wetting layer is larger than that of the island separation.

We can also exclude facet diffusion as the rate-limiting process. From the experiments reported here as well as others, the island sides are flat with the same facet slope regardless of annealing temperature (indicated by a constant number of single steps).[10] If facet diffusion was the controlling process allowing atoms to accumulate on the facet planes, we would have seen a decreasing facet slope with annealing time, implying an increase in the number of single steps at the island sides.

Note that we believe the barrier between the sixth and seventh layer diffusion has little affect on the growth of seven-layer islands. If this barrier was instead appreciable, the slow transfer of Pb from the sixth to seventh layer would lead to a long lifetime for six-layer islands, making them observable in either STM or the diffraction. From previous studies, as well as those reported here, we know that six-layer islands rarely form, indicating that the sixth layer is energetically less favorable than fifth or seventh layers. It therefore stands to reason that, once a sixth layer forms, a seventh layer of lower energy would form as well. We would expect little or no barrier for six- to seven-layer formation (it is certainly much smaller than the barrier for five- to six-layer formation). In other words forming six-layer islands is identical to forming seven-layer islands.

Below 175 K, in regions (i) and (ii), Fig. 5(a) indicates a different type of kinetics. At lower temperatures, $T = 160$ K, Fig. 5(a) shows that there is an increase of $\Delta A_5$ by approximately 3%. This is well below the maximum possible of 10% (0.5 ML/5) if all the material goes into building five-layer islands. In fact, above 160 K in regime (ii), Fig. 5(a) reveals that $\Delta A_5$ starts to decrease while the corresponding $\Delta A_7$ increases. These trends indicate that only part of the additional 0.5 ML of Pb moves to the sides of the existing five-layer islands. Either five-layer islands are dissolving or being incorporated into new seven-layer islands or the additional 0.5 ML of Pb is incorporated elsewhere in such a way as to reduce the apparent five-layer island coverage. As we will now show, it is the latter process, specifically the formation of small two- and three-layer islands between existing islands, that lead to the apparent decrease in five-layer island coverage.

To investigate where the missing Pb has gone after deposition in this temperature range we used STM to look at the island morphology. The STM experiments differ from the diffraction experiments described above in that they are annealing experiments. Initially 3 ML of Pb is deposited at $\sim 180$ K, resulting in the formation of a predominantly seven-layer island-height distribution. The surface is subsequently cooled to $\sim 133$ K where an additional amount of Pb ($\sim 1$ ML) is deposited. The temperature is then raised to an annealing temperature where an STM image is taken. Figure 6 summarizes these experiments. From 133 K to 167 K the additional Pb deposited has nucleated lower-height islands (two- or three-layers high) in the region between the seven-layer islands. While the initial seven-layer islands have the characteristic hexagonal fcc(111) shapes, the lower-height islands are smaller in diameter and have domed shapes. By $\sim 183$ K all of the smaller islands have vanished, leaving predominately seven-layer islands (and a few five-layer islands). It is these small islands that account for the apparent decrease of $\Delta A_5$ seen in the LEED experiments below 175 K. Instead of the five-layer coverage decrease in Fig. 5(a) being due to islands dissolving, additional interference terms in the diffraction caused by scattering from two- and three-layer islands cause an apparent decrease of the five-layer component in the $g(q_\perp^*)$ curve. Because we have not included terms in Eq. (1) proportional to $A_2$ and $A_3$, fits to the experimental $g(q_\perp^*)$ curves tend to underestimate $A_5$ when these small islands are present.

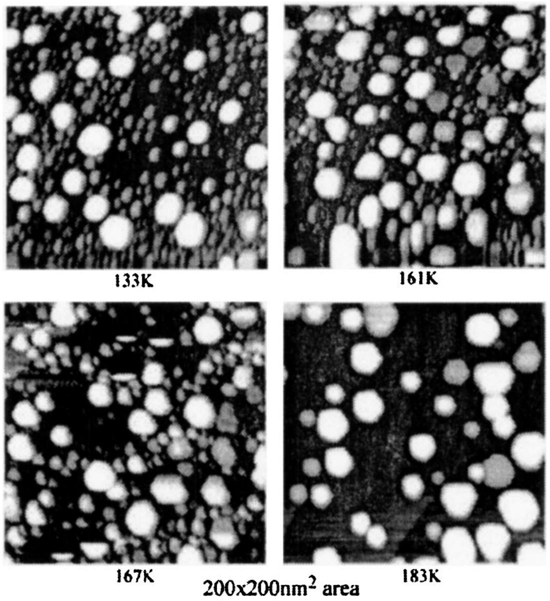

FIG. 6. STM images at four annealing temperatures. Brightest islands are seven-layers high. At 133 K small two- and three-layer islands have nucleated. By 161 K some five-layer islands have formed. By 180 K small islands have vanished, leaving predominately seven-layer islands.

A detailed analysis of the STM images reveals a number of important observations. First, a scan over a large 1 $\mu$m$^2$ area confirms that the predominant island height is seven layers, as deduced from the diffraction. No six-layer islands are seen. It is interesting to point out that if a smaller area is scanned repetitively, islands of larger height begin to form in bilayer increments up to as high as 13 layers. This indicates that the deposited Pb atoms in the second deposition are highly mobile, with their mobility possibly enhanced by the field between the tip and the surface. Second, as the additional Pb is annealed, it is transferred from the lower-height islands to the island tops. By 161 K some five-layer islands have formed and further annealing causes material in the interisland region to move to the tops of these five-layer islands to form new seven-layer islands. This process has a sharp onset temperature of $\sim 175$ K, consistent with the diffraction data.

Note that the STM results are also consistent with the diffraction experiment's conclusion that only part of the additional Pb is used to convert five-layer islands to seven-layer islands between 160 K$< T <$170 K. From Fig. 5(b) the five-layer islands' coverage above 160 K is less than 20% of the surface. This means that, although the additional Pb is sufficient to fully cover the initial area of the five-layer islands with two more layers ($0.5\ \mathrm{ML}/2=0.25\ \mathrm{ML}$) to build seven-layer islands, the measured increase in $\Delta A_7$ is less than this amount. This implies that only part of the added Pb moves to the top of five-layer islands with the rest moving to either the sides of existing five-layer islands or to the two and three-layer islands.

These results show that in the temperature range $150\ \mathrm{K} < T < 170\ \mathrm{K}$, with mostly five-layer islands present, three processes are in progress: (i) the transformation to seven-layer islands by adding two layers to existing five-layer islands; (ii) nucleation of two- and three-layer islands in the interisland region; (iii) the buildup of five-layers at the sides of existing five-layer islands. It is the competition between these processes that leads to the very sharp transition of the growth of seven-layer islands at $T\sim175\ \mathrm{K}$. In reality the latter process (iii) can be neglected. It is known from STM studies that sixth and seventh layer growth starts from material at the island edges.[17–19] Therefore, the completion of the seven-layer islands is predominantly accomplished by material diffusing on top of the freshly built five-layers around the island sides.

These results allow us a formalism to estimate the barrier for Pb to "climb" the five-layer islands and complete the seven-layer island formation. The transition temperature for seven-layer island growth is then determined by the competition between two processes; (i) atoms climbing to the top of five-layer islands to form the seven-layer islands (contributing to the increase of the seven-step area $\Delta A_7$) versus (ii) the nucleation of the two-layer and three-layer islands in the area between the islands. The probability, $p_7$, for the deposited Pb to grow new seven-step islands is given by $p_7 = \Delta A_7/\Delta A_7^{\max}$. Conversely, the probability to form two- and three-step islands is then $1-p_7$. These probabilities can be found from the time, $\tau_c$, required for an incoming atom to reach and climb the islands already on the surface versus the time, $\tau_N$, to nucleate a new two or three-step island in the surrounding region.

In an interval $\Delta t$ the faction $p_7$ of additional Pb atoms that grow seven-layer islands compared to those that lead to nucleation of smaller islands between the initial islands is given by

$$p_7=\frac{1/\tau_c}{1/\tau_c+1/\tau_N}. \tag{3}$$

To estimate the energy barrier for this process we use an argument similar to the one used by Krug *et al.* to describe the growth of islands by transport of material down over a step.[20] In our case we are interested in the opposite process of atoms ascending the island by going over the step-edge barrier. The time to reach and climb an island is

$$\tau_c=(S^2/4D_t)+(S^2/2Ra)\,\nu^{-1}\exp(\Delta E/kT), \tag{4}$$

where the first term in Eq. (4) is the time needed to reach the island and the second term is the time needed to "climb" the islands. $D_t$ is the terrace diffusion coefficient. The inverse of the second term in Eq. (4) is the probability to get to the top of the island, i.e., the product of the probability of an atom deposited between the islands to reach the island edges, $2\pi Ra/\pi S^2$, times the probability to overcome the barrier $\nu\exp(-\Delta E/kT)$, where $\nu$ is the attempt frequency to climb the island and $\Delta E$ the total barrier to climb the islands. Specifically $\Delta E$ is the energy difference between the energy minimum at a site outside the island to the saddle-point energy at a site on the edge of an island.

We need to compare $\tau_c$ to the time it takes to nucleate new islands, $\tau_N$. This is simply the time between deposition of two atoms in the surrounding area if diffusion on the wetting layer is considered "instantaneous:"

$$\tau_N=1/F\pi S^2, \tag{5}$$

where $F$ is the flux rate of incoming atoms.

The problem presented above is simplified in the sense that only two possible outcomes for a deposited Pb atom are considered; the Pb atom either reaches the seven-layer island or it nucleates to a smaller height island. We have neglected the possibility that the Pb atom can form a five-layer column at the sides of an existing island. However, this approximation is reasonable since the island separation determines the time to nucleate smaller-height islands, which is essentially the time to reach the sides of the five-layer islands.

Note that by 180 K any deposited atoms in the surrounding region either adsorb to the sides of the first five layers or reach the island tops, indicating that $\tau_c \ll \tau_N$. Also, the initial formation of islands at the growth temperature is as fast as the time it takes to deposit 4 ML of Pb (about 4 min), indicating that diffusion to the nucleating islands is essentially "instantaneous." Therefore, in the experiments reported here we can confidently neglect the diffusion term for the wetting layer in Eq. (4). With this assumption, we can now estimate $\Delta E$ using Eqs. (3)–(5). Taking the saturation value to be $\Delta A_7^{\max}=7\%$, $F=(1/60)\ \mathrm{ML\,sec}^{-1}$, $S=400$ Å, and $R=100$ Å, and assuming that the prefactor has the normal value $\nu=10^{13}$ Hz, we obtain $\Delta E=0.32$ eV.

Alternatively, within the approximation $\Delta A_5\sim0$, we can use all the $\Delta A_7$ data from Fig. 5 in the range $160\ \mathrm{K}\leq T \leq 180\ \mathrm{K}$ to put $p_7(T)$ into an Arrhenius form. This has the added advantage that the value of the prefactor is measured independently. This method gives $\Delta E=0.37\pm0.05$ eV and $\nu=1\times10^{15\pm2}$ Hz. This prefactor is slightly higher than $10^{13}$ Hz because of the assumption $\Delta A_5\sim0$. Below 170 K the assumption underestimates the ratio $p_7=\Delta A_7/\Delta A_7^{\max}$ that in turn overestimates the barrier and the prefactor ratio. Note also that $\Delta E$ estimated here is not the total barrier but the step-edge energy barrier, $E_s$, since we specifically assume that the diffusion barrier is nearly zero. We believe the edge barrier is at the top of the islands. Although we have no direct experiments to confirm this, material would have accumulated in front of the lower side of the islands at lower temperatures if the barrier was at the lower side. STM images do not observe such a buildup of material.

These estimates for the barrier reported here are not unreasonable. Estimates of the step-edge barrier for Ag(111) range from 0.22 eV by Bromann *et al.*[21] to 0.42 eV by Krug *et al.*[20] More importantly, estimates of the electronic energy differences between five- and seven-layer islands have been calculated and are estimated to be on the order of 0.05 eV.[9] The large step-edge barrier we find explains both the specific kinetic pathway and the sharp onset temperatures to the formation of a given island height in the phase diagram of Ref. 10. It also emphasizes that kinetics limitations are crucial in understanding the QSE island-height distribution.

## V. CONCLUSION

We have measured the change in five- and seven-layer QSE islands grown on Si(111) due to the addition of 0.5 ML of Pb. The experiments were done in a temperature range near the onset of seven-layer islands from five-layer islands. Between 165 K to 180 K we find that the additional Pb ''climbs'' existing five-layer islands to transform them to seven-layer islands. From the relative change in island area we are able to extract a barrier to seven-layer island growth in the limit of fast wetting-layer diffusion. We find that $\Delta E = 0.32 \pm 0.05$ eV and an attempt frequency of $\nu = 1 \times 10^{15\pm 2}$ Hz.

In recent STM studies of this system by Chang *et al.* the island formation kinetics were interpreted in terms of nucleation theory.[19] It is not clear, however, whether the scaling theory of nucleation can be applied in such a complicated system, even for the initial stage of island nucleation. Since only multilayer islands are seen on the surface and not the single-layer islands that could have formed according to nucleation theory (even at the lowest temperatures), we cannot infer that the observed multilayer island density is only determined by the initial nucleation. At least as we show in this paper, for $T < 180$ K the small islands in the region between the final stable islands dissolve, with their material transferring to the stable islands. This is an indication that, in addition to single-atom diffusion on top of the wetting layer, other microscopic processes can enhance mass transport to the islands i.e., a highly mobile lattice gas is present on top of the wetting layer. Islands shown in a scaling plot (as in Ref. 19) at higher temperatures ($T > 180$ K) have different heights and most likely different capture cross sections.

Our results for Pb/Si(111) show that, while minima in the electronic energy of these islands explains the bilayer heights, kinetic barriers are equally important in determining the height distribution. It is the interplay between thermodynamics and kinetics that gives rise to the kinetic phase diagram mapped in previous experiments.[10] Although islands of seven-layers are of the lowest energy and preferred for $\Theta < 7$ ML, they only form if the system is heated above 180 K. Otherwise the atoms do not have enough mobility to overcome the edge barrier $E_S \sim 0.32$ eV measured in our experiments.

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