A combined STM and SPA-LEED study of the “explosive” nucleation and collective diffusion in Pb/Si(111)

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ABSTRACT

A novel type of very fast nucleation was recently found in Pb/Si(111) with 4- to 7-layer high islands becoming crystalline in an “explosive” way when the Pb deposited amount in the wetting layer is compressed to $\theta_c \sim 1.22$ ML, well above the metallic Pb(111) density. This “explosive” nucleation is very different from classical nucleation when island growth is more gradual and islands grow in size by single adatom aggregation [8]. In order to identify the key parameters that control the nucleation we used scanning tunneling microscopy (STM) and spot profile analysis low energy electron diffraction (SPA-LEED). It was found that the number and duration of steps in iterative deposition used to approach θ_c and the flux rate have dramatic effects on the crystallization process. Larger depositions over shorter times induce greater spatial coverage fluctuations, so local areas can reach the critical coverage θ_c easier. This can trigger the collective motion of the wetting layer from far away areas to build the Pb islands “explosively”. The SPA-LEED experiments show that even low flux experiments in iterative deposition experiments can trigger transfer of material to the superstable 7-layer islands as seen from the stronger satellite rings close to the (00) spot.

I. Introduction

The competition between the surface and strain energy (due to lattice constant mismatch between the grown layer and the substrate) drives the morphological 2-d to 3-d transition in hetero-epitaxial growth commonly referred to as Stranski Krastanov (SK) growth mode. Below a critical thickness the growth is 2-dimensional but for larger film thickness the strain energy dominates and 3-d islands emerge. SK was observed in most of the experimental systems well above room temperature[1]. At high temperatures, thermodynamic parameters and the surface diffusion coefficient are sufficient to describe the transition and the island nucleation rate.

An analogous 2-d to 3-d transition has been observed in Pb/Si(111) and extensively studied in relation to Quantum Size Effects (QSE), but recently the emphasis has been the unusual findings of the speed of the nucleation process itself. In Pb/Si(111) strain is a key controlling factor (the lattice mismatch between Si(111) and Pb(111) is 11%). The 2-d transition from the Pb wetting layer to 3-d crystalline islands occurs well below room temperature at 180 K-240 K, with several novel observations that do not fit classical expectations [2-7].

After the Pb wetting layer is compressed to a critical coverage $\theta_c=1.22\text{ML}$ (22 % higher than the metallic Pb(111) density) fully completed crystalline islands emerge “explosively” out of the wetting layer [8], within an interval shorter than the STM acquisition time (irrespective of the size of the scanned area). As shown in ref.[8] the islands grow at higher growth rates than what is expected from classical nucleation theory and the material is transferred to the islands not by random walk adatom diffusion, but by the collective motion of the wetting layer over mesoscale distances. Clusters of neighboring islands were found to grow in the same direction with the islands adding material from the same side. In classical nucleation

islands grow independently and isotropically since material is added with the same probability from all sides. These directional correlations were seen to persist over long times confirming the collective motion of the wetting layer[8].

All these intriguing results are at great odds with classical nucleation[8-10]. Since there is still no understanding of their origin, it is important to carry out further experiments to determine other key parameters that play a role in this unusual type of nucleation. The current work shows how this “explosive” nucleation depends on the way Pb is deposited, i.e. on the number and duration of depositions to reach the same final amount and confirms the anomalous role of the flux rate (which is effectively higher for smaller number of depositions to reach the same total deposited amount). This effect can be thought off as hysteresis similar to what is commonly observed in first order phase transitions, since the transition is sharp for $\theta > \theta_c$ and depends on how material is added to the system. A new technique is applied SPALEED that probes these effects in an ensemble of islands. From the diffraction experiments similar conclusions are reached that faster mass transport is induced for smaller number of iterative depositions to deposit the same final amount or effectively for higher flux rates. When the wetting layer coverage reaches its critical value θ_c locally this triggers the “explosive” transfer of material to 4-layer and 7-layer islands. Such novel collective type of diffusion was also seen earlier in real time surface diffusion experiments of the wetting layer itself with low energy electron microscopy (LEEM). In these experiments diffusion was superdiffusive $x \sim t$ instead of random walk type $x \sim t^{1/2}$, consistent with the “explosive” nucleation observed with STM. The diffusion was non-Fickian since instead of a gradually spreading concentration profile from a steep initial profile at $t=0$, two oppositely moving but correlated steep concentration fronts were

observed . The concentration profile between the two moving fronts had concave instead of the classically expected convex shape[10].

Although several experiments have shown these striking features, the nature of this “explosive” nucleation is still not well understood and several controlling processes are unclear. The sharp transition at the critical coverage $\theta_c \approx 1.22$ ML is the most dramatic effect and it still remains mysterious how it triggers the correlated multi-atom diffusion over mesoscopic scale. What determines the locations where the island clusters have nucleated “explosively” and the directed flow of the wetting layer to feed these clusters from well outside the classically defined capture zones. The current experiments reveal additional information, since they suggest that large spatial coverage fluctuations exist within the wetting layer. In the local areas, where the wetting layer approaches θ_c , higher mobility and transfer of material from the outside region to the islands is initiated, and can trigger the abrupt nucleation.

II. Experimental

As described in previous work[9] we use two complementary techniques to study the growth. High resolution Spot Profile Analysis Low Energy Electron Diffraction (SPA-LEED) provides a statistical picture of the growth (i.e. averaging over 10^6 regions of coherent scattering on the surface). By studying the spot intensity distribution as a function of the normal and parallel momentum transfer components we can deduce detailed information about the island height, size, shape, etc . Variable temperature STM provides local information and directly confirms the structures from real space images.

The experiments were carried out in two different UHV chambers one equipped with SPA-LEED and the other chamber with an Omicron variable temperature STM[9]. Calibration of the deposition rate in the LEED chamber was based on Auger measurements carried out both at

room and low temperature. The flux rate in the STM chamber was determined by calculating the volume enclosed by the uniform height islands since both the height and size of the islands are known from the piezo calibration based on Si(111) step heights.. The temperatures were measured with Re-W (3%-25%) thermocouple spot-welded on the Ta clips holding the crystal in the LEED chamber and with a Si diode attached to the STM stage in the STM chamber.

III. Different kinetic pathways studied with STM to approach the critical coverage θ_c

Figures 1(a-c) show the very unusual nucleation of Pb islands after Pb stepwise deposition at $T = 224$ K and $F = 0.13$ ML/min. After three depositions (1.04 ML + 0.06 ML + 0.06 ML) for a total of 1.16 ML the result is shown in Fig. 1(a) over a scale 200×177 nm² with no islands present. The coverage is defined in terms of the metallic Pb(111) density (1 ML = 1.89×10^{15} Pb atoms per cm²). The density of the wetting layer can increase above the metallic density because the Si substrate facilitates the Pb adatoms to move closer than their average distance in bulk Pb [8]. Figure 1(b) shows the outcome after an additional incremental $\Delta\theta_i = 0.06$ ML deposition; fully completed multi-height (of 4 to 7-layers instead of 1-layer islands) perfect crystalline Pb islands, all above a minimum radius of ~ 35 nm, emerge. The island density is very low at 2×10^{-5} islands/nm². A smaller scale was intentionally used in Fig. 1(a) to try to capture structural changes in the wetting layer over the nano scale. It has been noted that some ordering is seen along the [110] direction and possibly is an indication of the onset of the correlated motion of the wetting layer. Such changes were seen in a different experiment shown in Fig.1(c) with $\theta = \theta_c = 1.22$ ML because a smaller amount $\Delta\theta_i = 0.015$ ML was used to bring the system closer to θ_c and thus trigger the “explosive” nucleation. Since it is not known where the “explosive” growth will occur it is not possible to place the tip and scan the area where islands will emerge.

According to the established nucleation theory one expects to observe nucleation of small 1-layer islands which subsequently should grow gradually both in size and height. Because the nucleation and the growth are stochastic processes, the islands are expected to exhibit a peaked island size distribution that also includes a large fraction of small islands [11-13]. This is not observed in Fig. 1(b). 15 islands have nucleated in the area of $1000 \times 1000 \text{ nm}^2$ with an average height of 4.6 layers (there are 4-, 5-, 6-, and 7-layer islands evolving to become the 7-layer superstable height [9]). The ratio between the amount of Pb in the islands $\Delta\theta_{\text{isl}}$ to the deposited amount $\Delta\theta_i \sim 0.06 \text{ ML}$ in the last iterative deposition step is $k = \Delta\theta_{\text{isl}}/\Delta\theta_i = 4.4$. In other experiments, k can be much higher depending on how close the coverage approaches θ_c , in the last deposition step $\Delta\theta_i$ prior to the emergence of the crystalline islands. Therefore material from the amorphous Pb wetting layer must have moved to the islands in addition to the amount that has been deposited during the last deposition step. The amount in the islands is much more than what was collected within the classical capture zones defined by the Voronoi cells surrounding each island.

These results are at odds with standard nucleation [2-7] because fully completed islands (and not gradually growing islands as expected from classical nucleation) are observed between the two successive images as shown in figs. 1(a) 1(b). Using nucleation theory to estimate the diffusion length from the average island separation (as universally applied if diffusion was classical) one deduces that the diffusion length must be at most $s = 220 \text{ nm}$. Using mass balance under the nucleation theory assumption that the material was collected from the material deposited during the last $\Delta\theta_i$ deposition step, we obtain a collection area surrounding each island which is much bigger than the corresponding Voronoi cells. The average volume in fig. 1(b) is 5300 nm^3 and the average height is 4.6 layers of the islands in fig.1(b) while the amount

deposited within the average island separation is $\Delta\theta_i\pi s^2$. Since one Pb adatom resides in a cell of area 0.1 nm^2 and the interlayer spacing of Pb(111) is 0.29 nm the above volumes can be converted into number of adatoms. The analysis shows that the collection area must be 4.2 times larger than the Voronoi cell area surrounding the average island. Since there is some range of island sizes these estimates will be larger for the larger islands especially the large 7-layer island in the middle of Fig. 1(b) that has also attained its equilibrium semi-hexagonal shape.

It is important to note that for a collection area 4.2 times larger than the Voronoi area, the collection areas of neighboring islands overlap, i.e., part of the Pb in the islands must also originate from the wetting layer. The nature of this long range correlation in the motion of the wetting layer is not fully understood; but as shown in ref.[8] clusters of neighboring islands grow by the same direction and with large shifts of their center of mass ($\sim 20 \text{ nm}$) as material is added suggesting the correlated motion spans mesoscale distances.

Despite the lack of theoretical understanding of the origin of this unusual mass transport, its intriguing character can be better seen by contrasting it with predictions based on classical diffusion and by relating it to the real time experiments of ref.[10]. The expectation that the growth of the islands is proportional to their Voronoi area is based on diffusion being carried out by the independently moving adatoms, with larger areas capturing larger number of adatoms. Diffusion of the wetting layer itself to refill an initial vacant area was found to be non-Fickian as seen in fig.3(c) of ref.[10]. Concave profiles $\partial c/\partial x > 0$ were mapped out outside the vacant area corresponding to mass accumulation (instead of the expected convex profiles $\partial c/\partial x < 0$ observed in concentration profile evolution experiments, which indicate mass depletion, as material moves from the outside to refill the vacant area). For the current nucleation experiments if one assumes that material added to an island must originate only from the wetting

layer within its Voronoi area, then this also implies the failure of Fick's law $J = -D\partial c/\partial x$. The flux within adjacent Voronoi areas will be pointing in different directions (towards the centers of the adjacent Voronoi areas where islands have nucleated). At the boundary shared by the two Voronoi areas the flux J (or $\partial c/\partial x$ if Fick's law was valid) should be discontinuous. Or equivalently the concentration $c(x)$ would not vary smoothly with distance x . This implies a more severe violation of Fick's law than the sign change of $\partial c/\partial x$ seen in ref.[10]. It is a different even more perplexing way, to express what was shown in refs. [8-10] that the wetting layer moves superdiffusively and not according to random walk diffusion.

Deviations are also seen in the island size distributions (of heights, areas, volumes) because for Pb/Si(111) the nucleated islands do not form gradually but emerge perfectly crystalline and completed. For all three size distributions the experimental data show that all observed quantities are above some minima and the distribution are highly asymmetric. The classically predicted histograms are expected to be peaked with a substantial fraction of small size islands below the histogram averages [11-13]. The classical distributions should have tails on either side of the average. The large discrepancy between the prediction that smaller islands should be a large fraction in the island distribution and the observation that island sizes larger than some minimum value are present, is a result of the "explosiveness" of this novel type of island nucleation.

Previous results about the "explosive" nucleation were presented in ref.[8] for slightly lower temperature $T=200$ K and $F=0.12$ ML/min. More importantly a larger number ~ 10 of sequential smaller deposition steps were used, after the first larger initial deposition at $\Delta\theta_1 = 0.82$ ML. The deposition steps were smaller than $\Delta\theta_1$ (the shutter was kept open for a few seconds corresponding to ~ 0.01 ML) to reach the critical coverage $\theta_c = 1.22$ ML with a finer

control. These experiments have also shown that the nucleation is abrupt and surprisingly clusters of neighboring islands grow from the same direction (seen in fig. 4 of ref.[8]). Mass is transported by the wetting layer from outside the classical capture zones similar to the previous Voronoi area analysis. However a major difference with the data of Fig. 1(b) is that the nucleation rate is lower although the island density and heights are similar. The average island diameter and k value in the experiment of Fig. 1(b) is twice the values in the experiment of Ref.[8]. As confirmed in other experiments to reach θ_c , “explosive” nucleation depends on the number and duration of the stepwise deposition sequence $\Delta\theta_i$ to reach θ_c . For smaller number of steps and longer deposition intervals (3 steps and $\Delta\theta_i \sim 0.06\text{ML}$ in the current experiment) larger transfer of material from the wetting layer to the islands is observed. One possible reason is that the larger deposition steps $\Delta\theta_i$ result in larger spatial variation in the deposited amount within the wetting layer and therefore it is easier to reach the conditions of critical coverage θ_c at specific location. These locations can generate the conditions for “explosive” nucleation and these is where the islands are seen.

Although the STM is not the ideal instrument to study kinetics because of the finite acquisition time, which is typically $\sim$ tens of seconds depending on scan size, one can safely conclude that the nucleation time is less than the STM acquisition time. This conclusion is also very consistent with earlier diffraction experiments with all surface diffraction techniques RHEED, X-ray and He-scattering[14-16] that have shown a step-like intensity increase of the Pb(10) spot, during deposition, after the completion of the wetting layer. The onset of regular RHEED oscillations indicating Pb crystallization, after irregular intensity variation (due to the wetting layer) is very sharp at even higher flux rates (0.9 ML/min) [14] and completion times of ~ 0.1 sec is deduced for island formation after a $\Delta\theta_i = 0.022$ ML deposition.

IV. SPA-LEED studies of mass transfer to superstable 7-layer islands at low flux rates.

The typical Pb(10) spot corresponding to the formation of Pb islands is seen in Fig. 2 after 2.2 ML Pb deposition on the 7x7 at $T = 180$ K. The spot position at 109 %BZ, as seen in many other earlier studies [9], proves the Pb islands are crystalline, unstrained, and with the same lattice constant 0.35 nm as bulk Pb. Using the Pb(10) spot to study the very early stage of nucleation requires a minimum number of Pb islands to form to have discernible Pb(10) intensity above the background level. Fig. 3 shows the evolution of the Pb(10) spot at $T = 202$ K and the abrupt intensity rise at 30 min of deposition which determines the flux $F = 0.03$ ML/min. The change of slope and the almost linear intensity increase is indicative of the very fast crystallization. Similar sharp rises were observed in other diffraction experiments monitoring in real time the growth mode of Pb/Si(111) at low temperatures[14]. As already noted this unusual process has features not expected in classical nucleation because of the sharp transition at θ_c . The use of the term “explosive” is based on ref.[8] with completed islands emerging when the critical coverage θ_c is reached. The linear time dependence of the observed intensity in fig.3 is consistent with the extremely fast “explosive” nucleation. The island growth involves two sequential processes, i.e., the time to deposit the atoms which is linear in time because the flux is constant and the time for the deposited atoms to reach the islands. Since the observed time dependence of the diffracted intensity is linear, the latter time must be negligible, as expected for the collective superdiffusion seen in the other Pb/Si(111) experiments refs. [8,10,19].

It is also possible to determine the emergence of the islands by monitoring the (00) spot intensity versus deposited coverage θ . The amorphous wetting layer which forms first exhibits very low (00) spot intensity and the onset of Pb crystallization is seen from the sharp rise of the specular intensity. This sudden increase of intensity during crystallization has been

observed both with RHEED[15] and SPA-LEED[17]. A more recent study of Pb/Ge(100) using Helium scattering[18] has shown that after completing the wetting layer with a critical coverage $\theta_c \sim 3$ ML the onset of Pb crystallization is signaled by similar abrupt slope change of the (00) spot intensity, which grows linear in time. This change indicates the formation of crystalline QSE-driven Pb islands.

Paradoxically the nucleation is more efficient at higher flux rate and a larger degree of crystallization is observed, despite the shorter diffusion time and diffusion length attained at high F (if diffusion in Pb/Si(111) was classical random walk of independently moving Pb adatoms). This is a different way to verify the importance of the compression in the wetting layer for the “explosive” nucleation to be initiated. The role of compression is also reflected in how the “explosive” nucleation depends on the “history” of the deposition, i.e., the duration and number of iterative deposition steps used to deposit a given coverage on the surface.

Such anomalous and unintuitive dependence on flux rate was first observed in X-ray diffraction experiments[19] studying the coarsening of the Pb islands due to QSE. The experiment monitors the evolution of the initial height distribution that includes unstable (even layer) and stable (odd layer) to superstable 7-layer islands over hours. The final height 7-layer distribution was sharper and the island density was lower when a high flux rate $F = 0.5$ ML/min was used (over $T = 200$ K - 240 K). If a lower flux rate was used 0.062 ML/min there was no coarsening and the initial island height distribution of 4- and 7-layer islands remain unchanged. These initial coarsening experiments are consistent with the previous discussion larger stepwise increments $\Delta\theta_i$ and/or higher flux rates trigger faster mobility in the wetting layer.

In light of the information collected from the STM experiments and the anomalous dependence on flux rate of the “explosive” nucleation we have also performed SPA-LEED

experiments to further identify this intriguing physical mechanism. Starting with the growth regime around θ_c , close to the point where the wetting layer can easily become more mobile when it is compressed by minute amounts, the nucleation was studied for different deposition pathways. Initially an amount of Pb atoms was deposited within few percent below θ_c followed by smaller $n \sim 10$ deposition steps with the shutter open for intervals either $\Delta t_i = 4$ min or $\Delta t_i = 2$ min corresponding to $\Delta \theta_i = 0.12$ ML or $\Delta \theta_i = 0.06$ ML iterative deposition steps. The final state had an amount of approximately ~ 1.22 ML added to the initial surface. A lower temperature of 180 K was used to ensure that it is possible to determine the island density from the satellite rings surrounding the (00) spot. The nucleated island separation distribution is expected to be a peaked function at the island average separation l which will result in the satellite (or sometimes refer to as Henzler rings) at wavevector $2\pi/l$.

A low flux rate $F = 0.03$ ML/min was used (lower than in the experiment of ref.[19]) thus ensuring that both the lower T and F should exclude coarsening through Ostwald ripening. Two electron energies were used, $E = 43.7$ eV an out-of-phase condition for 7-layers (and close to an in-phase condition for 4-layer height islands) and $E = 56$ eV an out-of-phase condition for 4-layer islands (but in-phase for 7-layer islands). These identifications are based on fig. 3 of ref. [20]. For example the energy 56 eV corresponds to a value of the electron scattering phase $S = \Delta k_z / (2\pi/d) = 3.62$ where Δk_z is the z component of the momentum transfer of the incident electron beam and d is the step height of Pb islands. At this out-of-phase condition of 4-layer islands destructive interference between the electrons scattered from the top and from between the 4-layer islands results in profiles most sensitive to the 4-layer island separation. By using distinct energies which are sensitive to different heights we can simultaneously monitor the evolution of the 4-layer and the superstable 7-layer islands.

According to classical nucleation theory the island density should start from zero and reach a constant value at steady state when the diffusion length of newly deposited Pb adatoms is comparable to the island separation, so the Pb adatoms can only join preexisting islands. Since the satellite ring wavevector k_{ring} is related monotonically to island density it should follow a similar dependence on deposition. In the SPA-LEED iterative coverage deposition experiments the opposite is observed. k_{ring} decreases with deposited amount which indicates an increasing island separation and therefore transfer of material (from the amount in the iterative coverage steps $\Delta\theta_i$ or from the wetting layer) to larger islands which grow to be further apart. This confirms a very active and highly mobile wetting layer.

The evolution of the satellite rings close to the (00) spot is seen in figs. 4 and 5 for coverages of 1.22 ML, 1.34 ML, 1.58 ML, 1.82 ML, 2.06 ML, and 2.3 ML obtained with iterative deposition steps $\Delta\theta_i$ (only 6 of the profiles are shown of the full set collected to reach the final 2.3 ML coverage). In fig. 4, the electron energies are $E = 43.7$ eV (blue), 56 eV (red) and in fig. 5 the electron energy is constant $E = 56$ eV but the iterative deposition steps were $\Delta\theta_i = 0.12$ ML (red) and $\Delta\theta_i = 0.06$ ML (green).

The results show that there is major mass transfer in the system after each iterative deposition step. Fig. 4 shows that there is more evolution in the distribution of the 7-layer islands, since for $E = 43.7$ eV the rings become more pronounced and the central component at $k_{\parallel} = 0$ drops. The ring wavevector k_{ring} decreases from 1.8 %BZ in the 1.34 ML profile (where the formation of the ring can be first discerned) to 0.8 %BZ at 2.3 ML. This suggests that the 7-layer islands are the larger fraction of islands and that their average separation changes from 22 nm to 48 nm (or correspondingly the island density decreases from 6.5×10^{-4} islands/nm² to 1.35×10^{-4} islands/nm²). For the $E = 56$ eV profiles (which measure changes in the 4-layer

islands), the rings are much weaker and at larger wavevectors. This finding is consistent with several earlier experiments[9,19] showing that the 4-layer islands are unstable, they exhibit a higher island density, i.e., smaller island separation, and eventually transform into superstable 7-layer islands. The stepwise coverage deposition $\Delta\theta_i$ triggers the unusual collective mobility of the wetting layer and shifts material to 7-layer islands. It is important to keep in mind that although the flux and temperature used are lower than the ones in Ref.[19], there is considerable evolution in the system[21]. Clearly the sudden and strong changes in the system induced by the stepwise iterative deposition not only show that 7-layer is the superstable height but reconfirm that the growth does not follow classical nucleation theory. This is only possible because of the unusual mobility discussed before in connection to the STM experiments showing the wetting layer is very active and highly mobile. These confirm the earlier real time experiments using LEEM in concentration profile evolution experiments of the wetting layer itself [10]. Furthermore at $E = 56$ eV the smaller fraction of 4-layer islands is at out-of-phase with both the wetting layer and the 7-layer islands. This explains the large remaining intensity at $k_{\parallel} = 0$ because the destructive interference is from the beating of two unequal terms, the area covered by the 4-layer islands and the much larger area covered by 7-layer islands or the bare wetting layer area. It follows there is no complete intensity cancellation.

From the profiles of fig.4 the average island size L can be deduced by using the island separation l and the known amount of deposited material on top of the wetting layer. Because the average area covered by the 7-layer islands is πL^2 the coverage can be written as $\theta = 7L^2/l^2$. Using the separation value $l = 48$ nm deduced for the final coverage $\theta = 2.3$ ML and the amount in the islands 1.08 ML, it follows $L = 18$ nm consistent with what is measured in the STM experiments[9]. The island size can be estimated for the first profile (when the satellite rings can

be barely discerned at 1.34 ML) with a wavevector of the satellite ring $k_{\text{ring}} = 1.8 \text{ \%BZ}$. Even if it is assumed that the Pb amount $\sim 0.34 \text{ ML}$ (all the amount in excess of 1ML the coverage of the uncompressed wetting layer) to be part of the islands it will only lead to island sizes $L = 5 \text{ nm}$. Under the assumption that the maximum amount of Pb has been transferred from the wetting layer to the islands and assuming uniform island density on the terraces, the average island size deduced with SPA-LEED is substantially smaller than 18 nm observed in the STM images. This is consistent with what was discussed earlier that fully completed islands emerge after the “explosion” and the island size distribution starts from a minimum island size. It further confirms the unusual “explosive” nucleation. For the islands to be 18 nm at this lower total coverage 1.34ML, the surface must be inhomogeneous with areas where clusters of islands with size 18 nm coexist with large vacant areas with no islands, so the total amount in islands on top of the wetting layer sums to 0.34 ML. The nucleation happens in areas where the wetting layer has locally reached the critical coverage θ_c while the vacant areas are the locations where the coverage is well below θ_c .

Further evidence for the unusual growth is seen in fig.5 where the comparison is made between stepwise iterative experiments for the same energy $E = 56 \text{ eV}$ but with $\Delta\theta_i = 0.12 \text{ ML}$ (red) and $\Delta\theta_i = 0.06 \text{ ML}$ (green). Both the amplitude of the satellite ring is weaker and the central spike is higher for $\Delta\theta_i = 0.06 \text{ ML}$ than $\Delta\theta_i = 0.12 \text{ ML}$. For classical nucleation theory the effect of changing $\Delta\theta_i$ should not be relevant, since the island density should be the same defined by the island density attained at steady state. But better developed satellites and suppressed central spike is seen for the larger $\Delta\theta_i = 0.12 \text{ ML}$ deposition steps than the smaller $\Delta\theta_i = 0.06 \text{ ML}$ deposition steps, reminiscent of the larger islands observed in Fig.1(b) than in ref.[8] because of the smaller number but larger duration of each deposition step. As discussed

before, larger deposition steps $\Delta\theta_i$ can generate local areas where it is easier to attain θ_c , thus triggering the “explosive” nucleation followed by the flow of material from areas well outside this nucleation region to provide the mass balance needed to build the islands.

V. Conclusions

The unusual “explosive” nucleation found for Pb/Si(111) at low temperatures was further examined to understand the controlling mechanisms. Using STM and SPA-LEED it is shown that the number and duration $\Delta\theta_i$ of sequential coverage steps and effectively the flux rate can affect dramatically the crystallization. Higher flux rate or longer deposition steps $\Delta\theta_i$ result in larger islands and faster evolution to the superstable 7-layer islands. Local areas within the wetting layer can reach the critical coverage θ_c which triggers the collective motion of the wetting layer from far away areas to build the Pb islands. The SPA-LEED experiments show that even low flux experiments can induce transfer of material to the superstable 7-layer islands as seen from the stronger satellite rings close to the (00) spot, for electron energy 43.7eV sensitive to the 7-layer island density. These experiments demonstrate the importance of the critical coverage θ_c and provide easy practical ways to predictably tune the outcome of the “explosive” nucleation.

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21. A phenomenological scaling law $n(t)=n_0t^\beta$ can be used to describe the island density change from the observed satellite ring change over the time of the experiment. This results to an exponent $\beta \approx 0.55$ higher than the Oswald ripening exponent $\beta \approx 0.33$ and considerably higher than the measured exponent in ref.[19] $\beta \approx 0.07$ despite the least favorable conditions of flux rate and temperature in the current experiments.

Figure captions

Fig. 1 Unusual “explosive” nucleation of Pb islands after iterative Pb deposition at $T = 224\text{K}$ and $F = 0.13 \text{ ML/min}$. (a) After 3 depositions ($1.04 \text{ ML} + 0.06 \text{ ML} + 0.06 \text{ ML}$) for a total of 1.16 ML over a scale $200 \times 177 \text{ nm}^2$ with no islands present. The coverage is defined in terms of the metallic Pb(111) density. (b) After the next $\Delta\theta_i \sim 0.06 \text{ ML}$ deposition fully completed multi-height crystalline islands are observed in an area of $1000 \times 1000 \text{ nm}^2$ with the amount in the islands $4.4 \cdot \Delta\theta_i$. (c) The wetting layer over a smaller scale $50 \times 50 \text{ nm}^2$ and with θ much closer to θ_c in a different experiment since it is not possible to know the location of an “explosive”

nucleation. Some ordering is observed along $[110]$ possibly indicating the onset of the collective motion of the wetting layer.

2. LEED pattern indicating the formation of Pb(111) islands from the streak spot. $E = 58$ eV, $T = 180$ K, $F = 0.03$ ML/min, and $\theta = 2.2$ ML (top right). Spot profile along the horizontal $[01\bar{1}]$ and $[10\bar{1}]$ 60° off horizontal direction showing the Pb(10) spot between Si(10) and Si-(7x7) $8/7$ spots.

Fig.3. The evolution of the Pb(10) spot at $T = 202$ K and the abrupt intensity rise at 30 min of deposition which determines the flux 0.03 ML/min. The change of slope and the almost linear intensity increase is indicative of the very fast crystallization.

Fig.4. The evolution of the satellite rings close to the specular spot for coverages (bottom to top) of 1.22 ML, 1.34 ML, 1.58 ML, 1.82 ML, 2.06 ML, and 2.3 ML obtained with iterative deposition $\Delta\theta_i$ at low flux rate $F = 0.03$ ML/min and $T = 180$ K. The electron energies are $E = 43.7$ eV (blue) $\Delta\theta_i = 0.06$ ML, 56 eV (red) $\Delta\theta_i = 0.12$ ML. The satellites for $E = 43.7$ eV an energy sensitive to 7-layer islands — are more pronounced and decrease with deposition, indicating transfer of material to larger 7 layer islands and lower island density. For classical nucleation no change of island density is expected.

Fig. 5. The evolution of the satellite rings close to the (00) spot for coverages (bottom to top) 1.22 ML, 1.34 ML, 1.58 ML, 1.82 ML, 2.06 ML, and 2.3 ML obtained with stepwise deposition

$\Delta\theta_i$ at low flux rate $F = 0.03$ ML/min and $T = 180$ K. The electron energy is constant $E = 56$ eV with stepwise deposition intervals $\Delta\theta_i = 0.12$ ML (red) and $\Delta\theta = 0.06$ ML (green). The stepwise deposition with $\Delta\theta_i = 0.12$ ML has better developed satellite rings and smaller central component at $k_{||} = 0$, indicating larger islands and therefore faster collective diffusion for larger $\Delta\theta_i$, as deduced also from the experiment in Fig. 1(b).

1(a)

1(b)

1(c)

fig.2

Fig.3

Fig.4.

Fig. 5.