Nonclassical “Explosive” Nucleation in Pb/Si(111) at Low Temperatures

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Abstract
Classically, the onset of nucleation is defined in terms of a critical cluster of the condensed phase, which forms from the gradual aggregation of randomly diffusing adatoms. Experiments in Pb/Si(111) at low temperature have discovered a dramatically different type of nucleation, with perfect crystalline islands emerging “explosively” out of the compressed wetting layer after a critical coverage \( \Theta_c \approx 1.22 \) ML is reached. The unexpectedly high island growth rates, the directional correlations in the growth of neighboring islands and the persistence in time of where mass is added in individual islands, suggest that nucleation is a result of the highly coherent motion of the wetting layer, over mesoscopic distances.

Keywords
temperature, condensed phase, critical cluster, directional correlations, Island growth, low temperatures, mesoscopics, materials science and engineering, Ames Laboratory

Disciplines
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Comments

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Nonclassical “Explosive” Nucleation in Pb/Si(111) at Low Temperatures

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Classically, the onset of nucleation is defined in terms of a critical cluster of the condensed phase, which forms from the gradual aggregation of randomly diffusing adatoms. Experiments in Pb/Si(111) at low temperature have discovered a dramatically different type of nucleation, with perfect crystalline islands emerging “explosively” out of the compressed wetting layer after a critical coverage Θc = 1.22 ML is reached. The unexpectedly high island growth rates, the directional correlations in the growth of neighboring islands and the persistence in time of where mass is added in individual islands, suggest that nucleation is a result of the highly coherent motion of the wetting layer, over mesoscopic distances.

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Nucleation is a fundamental process in nature that relates to a wide range of physical phenomena of both basic and technological importance in physical and biological sciences and engineering [1–6]. Many practical applications depend on the nucleation and growth of novel phases with unusual structural and electronic properties, relevant for catalysis and energy conversion. Nucleation involves the fine interplay between equilibrium and nonequilibrium physics, so it also relates to fundamental questions in statistical mechanics [7–12]. Although a complete understanding of nucleation has not yet been attained, the widely used paradigm is based on the model of classical nucleation. The main concept of the model is the existence of a critical size cluster rc, which defines the minimum cluster size, such that clusters larger than rc are stable and do not dissociate. The mass needed for the clusters of the condensed phase to grow is provided by diffusing adatoms within the initial homogeneous dilute phase. This analysis has been applied universally for a wide range of physical systems and especially to the epitaxial growth of ultrathin films [13–15].

In particular, island nucleation is observed in strained systems, a result of a morphological 2D-to-3D transition commonly referred to as the Stranski-Krastanov (SK) growth mode. The competition between strain energy (due to the lattice mismatch between overlayers and substrate) vs the surface energy drives the transition. Depending on the lattice mismatch ε between the substrate and the film different pathways are possible for the 3D transition. For small ε, 3D islands nucleate above a critical thickness hc with misfit dislocations decorating the interface, but for larger ε, roughening of the film is possible at much lower film thickness than hc [16]. For Pb/Si(111) no roughening is observed. These predictions have been fully confirmed in the prototype system Si1−xGex since ε can be varied extensively as a function of stoichiometry [16].

In all SK systems mass transport is through normal random walk diffusion. The detailed study of SK growth at lower temperatures and the role different nonthermodynamic factors can play are not fully explored. Pb/Si(111) follows a similar 2D-to-3D transition and strain is also a key factor (because of the 11% lattice mismatch between Si(111) and Pb(111) as in typical SK systems), but the transition occurs at ~150–250 K. In this work we show that a novel and faster type of nucleation dramatically different from classical nucleation is present. The novel nucleation is not driven by thermodynamic factors but by a very unusual type of mass transport. Pb(111) islands are not built gradually from the sequential aggregation of Pb adatoms; on the contrary, the deposited Pb adatoms are continually consumed by the wetting layer, which fully covers the substrate. After the wetting layer reaches a critical value Θc ≈ 1.22 ML [22% larger than the metallic Pb(111) density] nucleation is very abrupt, with multilayer, crystalline, fully completed islands, with at least ~105 atoms each, emerging from the compressed wetting layer. More importantly, mass transport is not the result of classical random-walk diffusion, but involves the collective motion of millions of atoms over mesoscopic scales. This striking result is deduced from the exceedingly high island growth rate when compared to the classical rate, from directional correlations in the growth of neighboring islands and from temporal correlations in the growth direction of individual islands. For Pb/Si(111) the temperature range these unusual phenomena are observed is centered at ~0.3Tm, with Tm the Pb melting temperature. Potentially such nucleation phenomena are more universal and not exclusive to Pb/Si(111) if the corresponding temperature “window” is scaled with Tm.
Experiments are presented here for Pb growth on the Si(111) – 7 × 7 substrate, and similar data have been obtained for growth on the Si(111) – Pb – α√3 × √3. Typical results are shown in Figs. 1 and 2. After an initial deposition of 0.82 ML at 200 K, Pb is deposited in smaller stepwise increments of Δθ ~ 0.045 ML (to approach Θc with a finer coverage control) and after each deposition, scans of large overlapping areas (their overlap identified by features on the steps) are taken to monitor nucleation changes. Nine images (the first eight are 500 × 500 nm² and the ninth 1500 × 1500 nm²) acquired consecutively are shown in Figs. 1(a)–(i) and no islands are seen [except two small islands nucleated at the step in Fig. 1(i)].

Figure 2 shows the result of one more 0.045 ML deposition in the area of Fig. 1(i). One normally expects to observe the nucleation of small one-layer islands which subsequently grow both in size and height. Because the nucleation and the growth are stochastic processes, the islands are expected to exhibit a wide size distribution that includes a large fraction of small islands. This is not what is observed. Large multiheight (of 4 to 7 layers instead of 1 layer islands) perfect crystalline Pb islands, all above a minimum radius of ~15 nm, emerge. The island density is very low at 1.65 × 10⁻⁵ islands/nm². The ratio k = (ΔΘisland)/ΔΘ of the Pb amount in the islands over the last amount deposited is 2.2, but in other experiments depending on the temperature T, or flux, or how close ΔΘ approaches Θc, k can be much higher. This indicates that the nucleation of the Pb islands is completed within the last short deposition in a very “explosive” way.

Although the STM is not the ideal instrument to study kinetics because of the finite acquisition time, which is typically ~tens of seconds depending on the scan size, one can safely conclude that the nucleation time is less than the STM acquisition time. This is seen from islands encountered earlier in the scan of any size having the same dimensions as islands encountered later in the scan; for fixed temperature the average island size is independent of scan size; under all scanning conditions only completed islands are observed both in the current experiments and in numerous previous experiments carried out by us using both STM and SPA-LEED to study quantum size effects

In Refs. [18–20] the authors have speculated that high diffusion must be present despite the low temperatures, but its puzzling character was assumed to be still classical. The character of the required mass transport responsible for the explosive nucleation has been identified with further STM experiments shown in Figs. 3(a) and 3(b). The temperature is 200 K and in Fig. 3(a) the coverage is Θ = 1.22 ML; the surface after 3 smaller depositions totaling 0.09 ML is shown in Fig. 3(b). Both imaged areas of Fig. 3 are very large, 1500 × 1500 μm², so mass transport can be checked over mesoscopic distances. Features along the step (i.e., inward kink bottom left) are used to match the y scales in the two images and
and in white in Figs. 3(a) and 3(b)]. This further supports that the wetting layer must be moving in a correlated way over large distances. The growth of neighboring islands can be used to estimate the distance \( l_0 \) over which the material arrives, by checking mass balance, with the main assumption that the amount added to the islands must equal the Pb amount increase within the surrounding area, after the small deposition \( \Delta \Theta \). Based on nucleation theory, the latter is the amount collected within the Voronoi area around a given island. Using, for example, the top left island of the five islands, its area increases from 1035 to 2151 \( \text{nm}^2 \), and it is six layers tall so \( 7 \times 10^4 \) Pb atoms are needed for its growth. Its Voronoi area is \( 4.3 \times 10^4 \text{ nm}^2 \) and has only collected \( 9.6 \times 10^3 \) atoms after the 0.022 ML deposition. This gives a ratio \( \sim 7 \) of the number of adatoms added to the available ones (if growth was isotropic), but since growth is directional the ratio is even higher, 14. This large difference indicates that material that was incorporated in the island must originate well outside its Voronoi area.

An average estimate that includes the growth of all the five islands within the outlined area \( A \) (of width \( w \approx 0.4 \mu \text{m} \) and length \( s \approx 0.6 \mu \text{m} \)) gives a quantitative estimate of \( l_0 \). The islands cover \( a \approx 0.03 \) A of \( A \) and the needed mass is proportional to the number of islands \( n = 5 \), their average height \( h = 4.6 \), and the measured average area increase \( \Delta a \approx 1.3a \). The supply to the outlined area \( A \) is through the narrow side normal to the growth direction and given by \( w l_0 \Delta \Theta \). Using \( \Delta \Theta = 0.022 \text{ ML} \) (i.e., the increase shown next in red in Fig. 4) \( s \approx 0.6 \mu \text{m} \), and \( l_0 = (1.3)(0.03)(hs)/\Delta \Theta \) gives \( 5 \mu \text{m} \), more than 3 times the imaged area.

This simple calculation is only approximate and under-estimates \( l_0 \) since it was assumed that no other islands are present in the supply area that feeds \( A \). Because other islands must be present, which will be encountered by the moving wetting layer and compete for Pb, \( l_0 \) must be larger than \( 5 \mu \text{m} \). Such diffusion distances are very consistent with the typical distances the wetting layer moves in step profile evolution experiments [21]. They are at least \( \sim 50 \) times larger than \( \sim 0.2 \mu \text{m} \) the diffusion length from the observed island density, if diffusion was classical and the scaling theory of nucleation is used.

Besides the spatial correlations in the growth of neighboring islands, there are also time correlations in the growth of single islands, which further confirm the nonstochastic motion of the wetting layer from far away. Analysis is shown in Fig. 4 where 4 islands within the area of Fig. 3(c) [marked by letters \( a, b, c, d \)] are analyzed to estimate their growth after six incremental depotions. The different colors correspond to amounts 1.220, 1.242 ML (used previously to estimate \( l_0 \)), 1.270, 1.310 ML [corresponds to Fig. 3(b)], 1.400, 1.490, 1.760 ML. [The island edges for the times shown in Figs. 3(a) and 3(b) are highlighted in white.] The inset shows the positions of the c.m. after each
depositions with vacuum area (a standard profile evolution experiment to the wetting layer mobility itself. The refilling of a circular LEEM has shown an even more intriguing result about adatom detachment barrier. A more recent experiment with magnitude than what is expected from the known Pb(111) The decay of the unstable islands was faster by orders of other systems where this unusual type of nucleation might be present.

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