Quantum stability and reentrant bilayer-by-bilayer growth of atomically smooth Pb films on semiconductor substrates

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Quantum growth of ultrathin Pb films on Ge(111) and Si(111) substrates is studied using scanning tunneling microscopy, total-energy calculations within density functional theory (DFT), and phenomenological modeling. Atomically smooth Pb films can be grown over *mesoscopic* length scales, but only above a critical film thickness of five or more monolayers. In the smooth growth regime, there exists an intriguing re-entrant bilayer-by-bilayer (RBBB) mode, characterized by strong preference for bilayer growth with periodic interruption of monolayer or trilayer growth. The salient features of the RBBB mode are attributed to the quantum nature of the film stability, as confirmed *quantitatively* in DFT calculations for Pb/Ge(111). The robustness of the quantum stability is further shown to originate from strong Friedel oscillations in the electron density within the Pb films.

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Because of its profound technological significance, fundamental understanding of metal and/or semiconductor interfaces has been an important objective in surface science and thin film growth. One active line of current research in this area is the exploration of quantum size effects on the stability and physical properties of metal overlayers on various substrates as the overlayer thickness shrinks to the nanometer scale. As a specific example, experimental studies of silver growth on GaAs(110) (Refs. 1 and 2) have led to the formulation of the so-called "electronic growth" model, emphasizing the quantum stability of ultrathin metal films.[3,4] Briefly, when the film thickness is only a few atomic layers to a few nanometers, the confined motion perpendicular to the film of the conduction electrons leads to the formation of two-dimensional (2D) subbands. Quantized motion of the many electrons may, in turn, lead to characteristic dependences of the total energy of the films on the film thickness, making certain film thicknesses more strongly preferred than others. Such quantum stability can be manifested by growth modes that otherwise would not be permitted on the basis of classical surface and interface free energy considerations.[5] More importantly, the existence of quantum growth modes, in principle facilitate the fabrication of atomically flat metallic nanostructures for devices that can operate in the quantum regime.

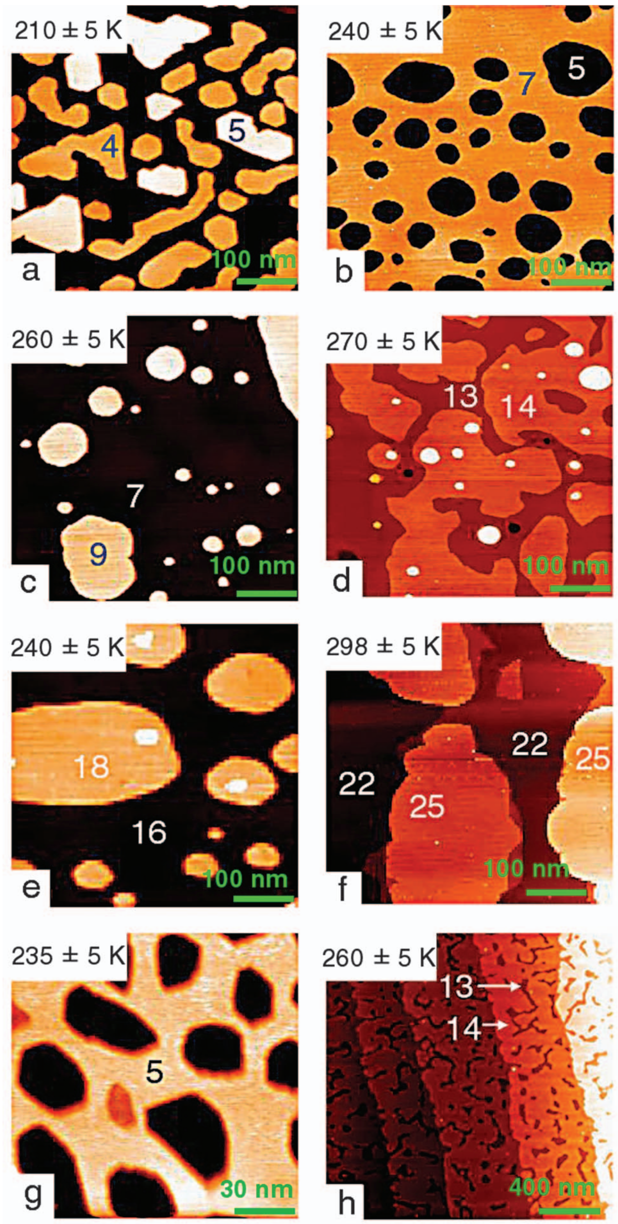
The morphological evolution of ultrathin Pb films on Si(111) arguably presents the most spectacular manifestation of quantum growth. Under proper kinetic growth conditions, Pb atoms organize into islands with atomically flat tops or "nanomesas."[6–10] The minimal island height is 4 or 5 ML, as measured from the wetting layer, while the island height increments are exactly 2 ML. Quantum size effects appear to be the underlying cause of this remarkable growth phenomenon. First-principles calculations have suggested that the 5-ML preferred height is a manifestation of "quantum phase separation"[11] while the bilayer increments in the layer thickness can be attributed to bilayer oscillations in the total energy of the films.[11–13] Theory and experiment also indicated that the substrate is a key factor in this growth regime. To elucidate the role of the substrate at the first-principles level, one would have to perform slab calculations which include the incommensurate Si substrate, a daunting challenge beyond the scope of current computing capabilities.

In this Brief Report we present a comprehensive and comparative STM study of Pb growth on three different types of Ge(111) and Si(111) substrates, along with first-principles calculations within DFT and phenomenological modeling for Pb films. Our STM observations show in real space that quantum growth is not just limited to nanomesas but can be exploited to produce atomically smooth Pb films over mesoscopic length scales on all the three substrates. The minimum coverage for smooth film growth, or critical thickness (t_C), is 5 ML. In the smooth growth regime, we establish the existence of an intriguing re-entrant bilayer-by-bilayer (RBBB) mode, characterized by strong preference of bilayer growth with periodic interruption of monolayer or trilayer growth. The existence of t_C and the salient features of the RBBB mode can be attributed to the quantum nature of the film stability, as confirmed *quantitatively* in DFT calculations for Pb/Ge(111). The Pb/Ge(111) system offers an example in which direct comparison can be made between experiment and DFT calculations with proper treatment of the substrate. The RBBB growth mode is further shown to be inherently connected to the Friedel oscillations of the film electron density with phenomenological modeling.

Pb was evaporated onto the Ge(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb($\alpha$), Si(111)$(\sqrt{3}\times\sqrt{3})R30°$-Pb($\alpha$), and Si(111)$(7\times7)$ surfaces in ultrahigh vacuum (UHV), using an effusion cell. The deposition rate (ranging from 0.25 to 0.33 ML/min) was calibrated with Rutherford backscattering spectrometry. The $(\sqrt{3}\times\sqrt{3})R30°$-$\alpha$ phases of Pb on Si(111) and Ge(111) were prepared by depositing 1/3 ML of Pb (in substrate units) on top of clean Si(111)(7×7) and Ge(111)$c(2\times8)$, respectively, following well-established procedures.[14,15] Continuous Pb films were deposited onto the 7×7 or α-phase substrates at a temperature of 150 K or less. The films all assume the (111) orientation; accordingly, we define a monolayer as the atom density of a closely packed Pb(111) plane. The low-coverage α phase first converts into the dense β phase[14,15] before multilayer growth commences. The films were subsequently annealed and studied *in situ* with a variable-temperature STM. The optimum annealing temperature for smoothing the film depends on the substrate and on the layer thickness, and ranges from 200 K to 300 K.

Numerous STM images have been recorded to monitor the various stages of growth. Here, we can only present a sampling of the images that illustrate the key points. Generally, as-deposited films (150 K) are quite rough and up to five different layer heights were observed at the growth front by STM (not shown). Upon annealing to ~200 K, the Pb atoms acquire sufficient mobility to smoothen the films. Figure 1(a) shows a 500×500 nm STM image of a Pb film. Flat-topped islands rising 4 or 5 ML above the wetting layer can be seen; no other island heights have been observed.[16] Atomic resolution images in between the islands (not shown) confirmed the ($\sqrt{3}\times\sqrt{3}$) structure of the β phase wetting layer. In this coverage range, Pb islands never merge to form a continuous film. In the following discussion, the layer count excludes the wetting layer (unless otherwise stated), so as to be consistent with the convention in previous studies of flat-top Pb islands.[6–8]

Figure 1(b) shows a 500×500 nm image of an almost continuous 7-ML Pb film with 2-ML deep voids. It is clear that in this coverage regime, the 5-ML film is atomically flat and continuous on a mesoscopic length scale while the larger part of the 5-ML surface is covered with an additional bilayer of Pb, making the total film thickness to be 7 ML. The 5-ML and 7-ML terraces neither possess single monolayer steps nor single monolayer voids, thus confirming the onset of perfect bilayer growth on top of the closed 5-ML film. Although 5-ML and 7-ML-high flat-topped islands have been seen before by STM,[6–8] the present result is a real-space demonstration of *continuous film growth proceeding in bilayers*. Figure 1(c) reveals 2-ML-high islands on the 7-ML films. Again, the absence of voids or monolayer high islands on the 7-ML film shows that the growth proceeds in a perfect bilayer-by-bilayer mode. Bilayer growth continues until the coverage reaches 13 ML. Figure 1(d) shows a 13-ML-high film with monatomic-layer high islands (14 ML) residing on top, and tiny amounts of 16-ML-high islands. Amazingly, after this intermission, near-perfect bilayer growth resumes at 14 ML, ending at 22 ML. Figure 1(e) shows the bilayer height steps on a 16-ML film. Figure 1(f) shows 3-ML-high steps on top of a 22-ML-high film, indicating a *trilayer* intermission. In summary, Pb grows in a perfect bilayer-by-bilayer mode from 5 ML to 13 ML and from 14 ML to 22 ML. Evidently, odd-numbered layers are favored between 5 and 13 ML while even-numbered layers are favored between 14 and 22 ML. As we will show, this RBBB growth mode is a manifestation of the quantum size effect (QSE) and the even-odd crossover phenomenon is the result of a beating of the interlayer spacing d_0 (2.86 Å) and the Fermi wavelength



Interface	Observed Layer Thickness										
Si(111)7x7-Pb	5	7	9	11	13	14	16	18	20		
Si(111)($\sqrt{3}\times\sqrt{3}$)-α	5	7	9	11	13	14	16	18	20	22	25
Ge(111)($\sqrt{3}\times\sqrt{3}$)-α	5	7	9	11	13	14	16	18	20		

FIG. 1. (Color) STM images of Pb on (a–f) Si(111)($\sqrt{3}\times\sqrt{3}$)$R30°$-Pb, (g) Ge(111)($\sqrt{3}\times\sqrt{3}$)$R30°$-Pb, and (h) Si(111)7×7. Layer thicknesses are indicated in each panel and are measured with respect to the wetting layer. The table summarizes the observed thicknesses for each interface with even-odd crossovers indicated in bold italics. Image sizes and postannealing temperatures are also indicated in (a–h).

$\lambda_F/2=1.99$ Å, which are slightly incommensurate.[11] The resulting beating periodicity of 9 ML implies even-odd crossovers not only between 13 and 14 ML, but also between 4 and 5 ML, and between 22 and 23 ML. The latter agrees with the observed trilayer step at 22 ML. Evidence for a 4–5 ML crossover is provided by the coexistence of 4-ML- and 5-ML-high islands at nominal coverage <4 ML [see Fig. 1(a)]. However, we never observed continuous films of 4 ML or less.[17]

Figure 1(g) shows a smooth 5-ML film of Pb on the β phase of Ge(111) with 5-ML-deep voids that go all the way down to the β-phase wetting layer. Upon subsequent deposition, the voids close before bilayer growth commences. Again, a minimum of 5 ML is needed to initiate smooth bilayer film growth on the β-phase substrates of Si(111) and Ge(111), indicative of a *critical thickness* t_C=5 ML (wetting layer excluded). The even-odd crossovers also occur at the same location as for Si, indicating that the smaller band gap for electron confinement on Ge does not alter the bilayer growth and stability crossovers of the films. The results of Pb growth on Si(111)7$\times$7 are similar. The even-odd crossovers occur at exactly the same locations as for growth of the other two substrates. Figure 1(h) shows a 14-ML-high film with monatomic-layer-deep voids, taken at the coverage where the second crossover takes place. Notice the very large scale of this figure. Evidently, it is possible to grow atomically flat Pb on Si(111)7$\times$7 on a mesoscopic length scale with a smoothness limited only by the terrace width of the silicon substrate.

Although oscillations due to QSE have been observed in island heights at coverages less than 9 ML,[6–8] the most astonishing result of the present study is that QSE in Pb is a very robust phenomenon and produces atomically flat films over mesoscopic distances, all the way up to 25 ML (possibly even further), and at fairly high temperatures. As shown below, the robust RBBB growth is almost perfectly reproduced in our extensive first-principles DFT calculations of the thickness-dependent film energy for the case of Pb on Ge(111). In these calculations, the Pb(111) films are placed on a *bulk truncated* Ge(111)($\sqrt{3}\times\sqrt{3}$)$R30°$ superlattice. This supercell perfectly matches a 2$\times$2 supercell of bulk Pb(111) after expanding the Ge lattice by only 1%. The artificial introduction of the 30° rotation thus enables us to accommodate the lattice mismatch between Ge and Pb. Applying the same trick for Si in a parallel orientation would require a 9% compression and results in a metallic substrate.[12] The DFT calculations are performed using the Vienna *ab initio* simulation package (VASP), based on the Perdew-Wang 1991 version of the generalized gradient approximation for exchange-correlation energy and ultrasoft pseudopotentials, with the Pb d orbitals treated as core states.[18] The Pb/Ge(111) system is modeled by a 2$\times$2 Pb supercell and a 10-layer Ge(111) $\times$($\sqrt{3}\times\sqrt{3}$)$R30°$ substrate. The Ge atoms located at the bottom layer of the slab are saturated with hydrogen, followed by a vacuum layer of 19 Å. The in-plane lattice constant of the Pb(111) slab is restricted to its theoretical bulk value (3.56 Å), while the layer spacings in the film thickness direction are fully relaxed. A default plane wave cutoff energy of 150 eV and 6$\times$6$\times$1 k-point sampling in the surface Brillouin zone are used in the calculations. Energy convergence is reached when the forces on the relaxed atoms are less than 0.01 eV/Å.

The stability of a thin film can be determined by its thickness-dependent surface energy.[3] The bulk energy should be perfectly linear in the film thickness N and is found from a linear fit to the computed total energy of the slab for large values of N. The surface energy of an N-layer Pb film (N <25 ML) is obtained by subtracting this bulk energy from the computed total energy of the slab.[3] The film is stable if the surface energy[19] satisfies

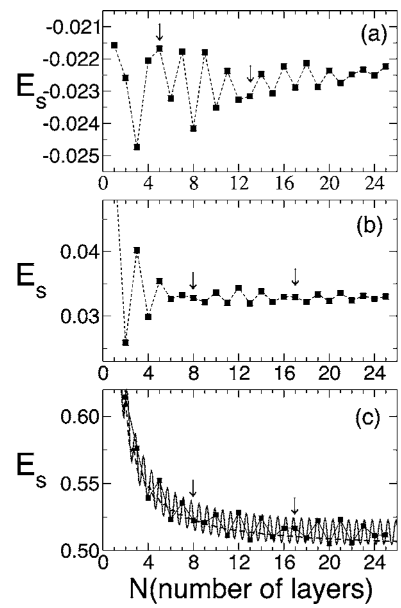


FIG. 2. (a) Thickness-dependent surface energy E_S (in eV/Å^2) of Pb(111) films on Ge(111). (b) Same as in (a), but for free-standing Pb(111) films. Note 100 that the layer numbers in (a) and (b) differ by 1 from the layer numbers in Fig. 1, due to the presence of a wetting layer in Fig. 1. The arrows indicate even-odd crossovers. (c) Surface energy E_S of a free-standing Pb film calculated using a simple "electrons-in-a-box" model with a constant background potential (dashed line) or a corrugated background potential (solid line). The oscillation amplitude ν of the corrugated potential, $V_{\rm el}(x)=-\nu\cos(2k_F x)$, is taken as 0.08 E_F (E_F=9.47 eV). The solid squares sample the discrete layer thicknesses, and the surface energies are given in units of $E_F k_F^2/4$.

$$2E_s(N) < E_S(N-1) + E_S(N+1), \tag{1}$$

where N is measured against the Ge substrate (namely, including the wetting layer). The $E_S(N)$ of Pb on the Ge(111) substrate are shown in Fig. 2(a); they are almost in complete agreement with the experiment, including the presence of the bilayer oscillations and the approximate locations of the stability crossovers (indicated by the arrows). According to Fig. 2(a) and Eq. (1), the stable heights are 5, 7, 9, 11, 12, 14, 16, 18, 20, and 23 ML *above the wetting layer*. These numbers nicely agree with the STM observations in Fig. 1. There is a small discrepancy in the precise location of the even-odd crossover, however. Experimentally, we observe the 13-ML film instead of the predicted 12-ML film. Likewise, we observed a 22-ML film instead of the predicted 23 ML. Interestingly, the calculations even reproduce the trilayer intermission seen in experiment. The calculated minimum at 3 ML appears to be the only other feature that is inconsistent with experimental observations. Note, however, that the atomic arrangement of the Pb films below 5 ML is not known.[16]

Despite the remarkable agreement between the experimental observations and DFT calculations for Pb/Ge(111), we have yet to fully understand the underlying mechanism for the robustness of the RBBB growth mode. For this purpose, we have also computed the surface energies for free-standing Pb(111) films, as shown in Fig. 2(b).[11] Such calculations show that the RBBB growth mode also exists in free-standing films but the even-odd crossover positions have shifted to 8 ML and 17 ML. The distance of 9 ML between the two crossovers remains the same, indicating that the effect of the substrate is mainly to "phase shift" the crossovers. Therefore, to look for the physics behind the robust RBBB mode, we can focus on free-standing films, avoiding complications caused by the substrate.

For free-standing films, because the existence of the two surfaces will induce Friedel oscillations in the electron density within the films,[20] it has been conjectured that the oscillatory nature of the quantum stability is related to the interplay between the Friedel oscillations in the electron density and the discrete nature of the lattice spacings.[3,11–13] In the following we elucidate how such Friedel oscillations in electron density can affect the film stability, which in turn results in the RBBB growth as observed. First, we model the system as a 2D Fermi gas with a corrugated background potential $V_{el}(x)=-\nu\cos(2k_F x)$, confined between two hard-wall potential barriers, where $k_F=1.58$ Å^{-1} for Pb along the (111) direction, and ν is a parameter measuring the magnitude of the oscillatory potential induced by the Friedel oscillations in the electron density. The corresponding surface energies are shown in Fig. 2(c). For a constant background ($\nu=0$), there are no apparent oscillations in the surface energy (dashed line),[21] showing that discretization of the kinetic energy spectrum alone does not induce robust oscillations in the quantum stability of the films. Oscillations in film stability appear when turning on the $2k_F$ potential (curved line), with the solid squares sampling the energies for discrete layers. Remarkably, these discrete energies clearly indicate the existence of RBBB growth. This simple model calculation even reproduces the crossover locations obtained in DFT calculations of free-standing films. Friedel oscillations decay toward the interior of the film, hence classical layer-by-layer growth should ultimately prevail for thicker films.[9]

In summary, we have presented real-space observations of a re-entrant bilayer-by-bilayer (RBBB) growth mode of Pb on three different substrates of Si(111) and Ge(111). The choice of the Ge(111) substrate enabled quantitative comparison between experimental and theoretical studies of quantum growth and assessment of the role of the substrate at the first-principles level. The RBBB mode of Pb is clearly a manifestation of the accidental near commensurability of the Fermi wavelength ($\lambda_F/2$) and the interlayer spacing d_0. Friedel oscillations were invoked to explain the robust quantum growth up to 25 ML. DFT studies addressing the relative magnitudes of the kinetic energy, potential energy, and exchange-correlation contributions to the QSE oscillations are currently underway.

Note added: Recently we became aware of Ref. 22, in which Pb films exhibiting oscillatory superconducting transition temperatures were grown on Si(111).[22]

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[16] Based on our thickness calibration, the density of the Pb layers below 5 ML appears to be ~20% less than that of bulk Pb. Once the bilayer growth sets in (>5 ML), the density of Pb equals that of bulk Pb, as determined from the relative area fractions of the flat terraces and 2-ML voids/islands in the STM images.
[17] Occasional observation of a single monolayer island or void is attributed to kinetic limitations.
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[19] There is no division by 2 for the surface energy as in Ref. 11.
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