Competing Classical and Quantum Effects in Shape Relaxation of a Metallic Island

Hiroshi Okamoto,[1,*] Dongmin Chen,[1,†] and Toshishige Yamada[2]
[1]*The Rowland Institute at Harvard, Harvard University, Cambridge, Massachusetts 02142*
[2]*NASA Ames Research Center, Moffett Field, California 94035*
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Pb islands grown on a Si substrate transform at room temperature from a flattop facet geometry into an unusual ring shape. The volume-preserving mass transport is catalyzed by the electrical field from the tip of a scanning tunneling microscope. The ring morphology results from the competing classical and quantum effects in the shape relaxation. The latter is enhanced by the large anisotropy of the effective mass, and leads to a sequential strip-flow growth on alternating strips of the same facet defined by substrate steps, showing its dynamical impact on the stability of a nanostructure.

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Structural stability of a nanostructure is of both fundamental interest and practical importance. In general, growth processes, such as vapor deposition, can be far from equilibrium and postdeposition transformation of a metastable structure into a thermodynamically equilibrium shape will take place if kinetic barriers can be overcome. This tendency is heightened for nanoscale structures as the surface/volume ratio increases. For a large strained structure, its stability can be well described by the balance between surface tension and the bulk elastic energy based on classical continuum theory [1,2]. It has become increasingly evident that quantum size effect (QSE) also plays a significant role in shaping a nanoscale structure. For instance, QSE is shown to be responsible for the reversal transition from three-dimensional to two-dimensional growth of Ag on a GaAs surface at some critical coverage [3], the bifurcation of a Ag film from N to $N \pm 1$ monolayer at an elevated temperature [4], and for the preferred height distribution and oscillating layer relaxation for lead (Pb) islands grown on silicon substrates [5,6].

In this Letter, we shall demonstrate that QSE plays a competing role alongside the classical thermodynamic effect in the shape relaxation of a small metallic island. Together, these effects transform a Pb island grown on Si(111) substrate from its initially flattop faceted morphology to a peculiar ring-shaped island, a process catalyzed by the electric field from a scanning tunneling microscope (STM) tip. Furthermore, QSE leads to a novel *strip-flow* growth and *double-step* growth on selective strips of the plateau inside the ring, defined by the substrate steps more than 60 Å below. It appears that atoms diffusing on the plateau can "sense" the quantized energy states inside the island and preferentially attach to regions that in turn reduce the surface energy, limiting the growth and stabilizing the ring shape. The ring shaped metal island had been observed previously, but no explanation has been given [7,8]. We propose a mechanism below to address this puzzling ring structure. There exist other ring shaped systems, such as imbedded GaInAs ring in a GaAs matrix [9], or the dried solvent which can be explained solely in classical terms [10].

The experiments were done using a homemade low temperature UHV STM system described elsewhere [11]. The base pressure of the STM and the sample preparation chambers is typically 3×10^{-11} Torr. N type Si(111) substrates (phosphorous doped, 0.05–0.06 Ω cm) are flashed to 1150 °C to obtain clean 7×7 reconstructed surfaces as checked by the reflection high energy electron diffraction. After the substrate cools down to room temperature, Pb is deposited onto the Si for 10 min from a crucible held at ~500 °C. STM images were normally taken at a tip bias of -2 V and tunneling current of 0.8 nA. Most experiments were done at room temperature (RT) unless indicated otherwise.

Pb on Si adopts the Stranski-Krastanov growth mode and (111)-oriented islands start to grow after the completion of two wetting layers [12]. Following the deposition at below and near room temperature, Pb islands are well faceted and their tops are atomically flat even when an island spans over several Si steps, forming a nanoscale wedge [13]. These islands are stable at liquid nitrogen temperature but efficient mass transport can occur at room temperature. A low energy electron microscopy (LEEM) study has shown that, due to kinetic effect, the growth of Pb islands proceeds layer by layer, and QSE becomes important as the system approaches equilibrium [14].

In this Letter, we focus on the postdeposition relaxation process of Pb islands. It is found that at RT the initially flattop Pb islands relax into an unusual ring shape as exemplified in Fig. 1. The ring islands possess a few characteristic features. The outer wall of the ring is well faceted while the inner wall is round, especially for smaller islands. As shown in Fig. 1(b), the central opening does not go all the way down to the wetting layer, but stays close to the original island height and evolves via a *strip flow growth* as we shall see below.

Similar to a previous report [15], we found that as the STM tip scans across a Pb island, the initially top-flat

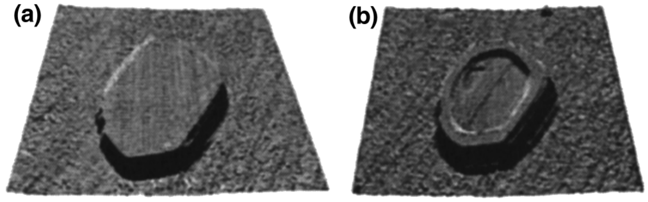

FIG. 1. STM images (8000 Å × 8000 Å) showing an initially flattop Pb island (a) grown on Si(111) transforming into a ring shape (b). The height of the flattop island (a) is ~60 Å. The height of the ring is about 25 Å measured with respect to the plateau of the central opening which is roughly at the same height as the flat island (a).

island is quickly transformed into a ring shaped island, even just by a single scan. Once shape transformation is "triggered," the further change of the island shape will proceed regardless of whether the STM tip continues to scan the same area. On the other hand, several days after the Pb deposition, we find ~70% flattop islands in areas that have not been scanned before. At liquid nitrogen temperature, however, tip-induced Pb island shape transformation is greatly suppressed and only flattop islands are observed. Similar ring-shaped islands of Pb on Si(100) have also been observed using either STM or LEEM [8]. Thus, the local electrical fields from the STM tip mainly serve to catalyze the process [16].

Figure 2 captures the transformation process of a small ring island. These STM images were taken sequentially at 3 min apart (including 20 sec scan time). Figures 2(b-1), 2(b-2), and 2(b-3) show the cross section extracted from the three images, respectively. Initially, Pb atoms along the perimeter diffuse to the top of the island and attach preferentially along the outer edge of the top terrace, forming the nucleation of the ring. The ring subsequently grows quickly upward and inward. Notice that the height, H, of the central plateau inside the ring increases by a very small amount from the height of the initial flattop island, even when the ring is nearly closed up [$d \rightarrow 0$, see Fig. 2(b-3)]. In our experiment, the island density is very low ($\sim 1/10\ \mu m^2$), and the shape transformation appears to be volume preserving. The island grows taller (h being as much as H) at the expense of a reduced lateral size. Notice that majority of the mass is transformed from the lower side of the island as marked by the arrows in Figs. 2(a-1), 2(a-2), and 2(a-3). Typically, Pb islands have a very small aspect ratio, $(H + h)/D$. The relaxation tends to increase the aspect ratio and yields more compact islands.

The above behavior also holds for large islands with D typically doubled or tripled but H increased only by 10%–20%. Since D is very large to begin with, the interior of the ring remains widely open for several days. Here STM reveals yet another unusual *selective strip-flow* growth process on the plateau inside the ring. Figure 3 shows a series of images of the plateau acquired consecutively at 3 min apart. In these images the Si

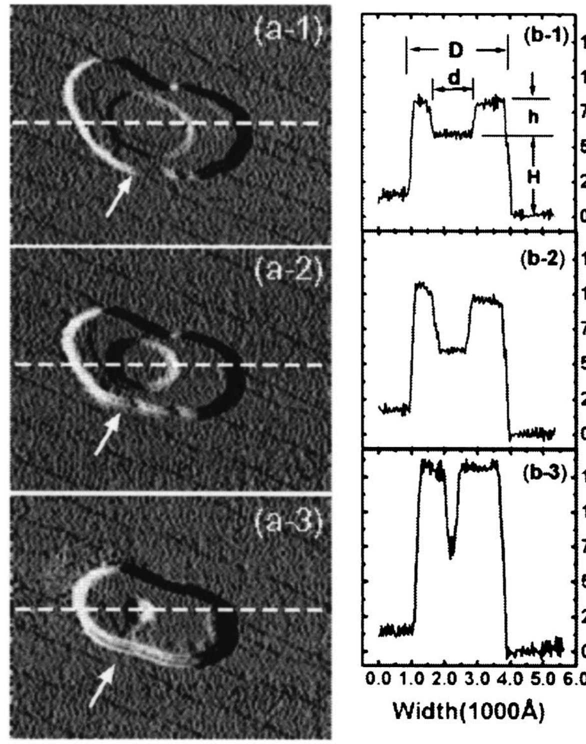

FIG. 2. (a) Sequentially recorded STM images (6000 Å × 6000 Å) showing the relaxation of an island shape in three minute steps. (b) Respective cross sections along the dashed line on the images.

substrate covered by Pb wetting layers descends from the lower left towards the upper right corner. Thus, the number of Pb monolayer N between the plateau and the substrate increases successively from lower left to upper right. In Fig. 3(a), two patches of a new layer above the same substrate step are growing towards each other from the opposite side of the inner wall of the ring. We refer to this as the Nth strip to indicate that it is on top of N Pb layers. As we proceed to Fig. 3(b), the Nth strip nearly completes. Quite surprisingly, now the $(N + 2)$th strip also starts to grow in the same manner, bypassing completely the $(N + 1)$th strip. As the $(N + 2)$th strip nears completion, the$(N + 4)$th strip begins to grow, again bypassing the $(N + 3)$th strip [Fig. 3(c)]. Notice that now the $(N + 1)$th strip also starts to grow, but with two layers at once (see the inset). The growth rate of the double layer strip is much slower than that of the single layer strip. Consequently, Fig. 3(d) changes very little from 3(c). I-V measurements were carried out on half-grown strips, and the results show that the strip growth shifts the level of the highest occupied quantum state (QS) away from the Fermi level (E_f) [13].

The shape relaxation processes unveiled above are drastically different from the layer-peeling relaxation process observed for a large hemispherical Pb island [17], and do not seem to fit to any established mechanism. The classical continuum theory shows that a strained system energetically favors wavy over flat film morphology,

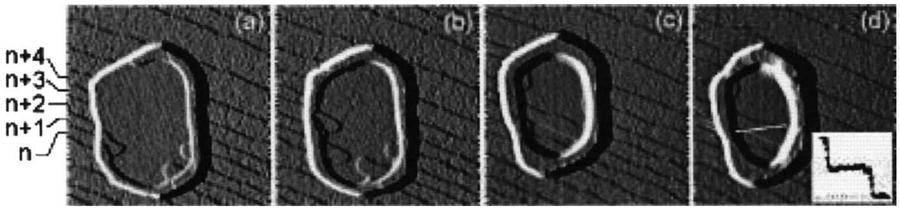

FIG. 3. Sequentially recorded STM images (8000 Å × 8000 Å) showing a sequential strip-flow growth on alternating strips on the plateau inside the ring. The inset shows the step height profile along the white line in (d).

for the increase of the surface energy is more than compensated by the reduced bulk elastic energy due to the surface undulation [1]. In the present experiment, the fact that the Pb islands transform ultimately to a more compact shape (Fig. 2) and that the mass transfer occurs preferentially from a region subject to greater stress implies that the shape relaxation is driven by similar thermodynamic forces. However, during the initial stage of ring formation, there is a rapid increase of surface to volume ratio in the ring portion, which contradicts this classical argument. Furthermore, the round geometry of the inner wall of the ring suggests that Pb atoms diffuse rather freely across the interior plateau so that formation of the ring shape is not a diffusion limited kinetic effect.

Let us now address the sequential strip-flow growth occurring on the plateau inside the ring. Previous studies have shown that a set of QSs (or subbands) exists for islands with thicknesses from 4–15 layers [6,13,18]. The number of the total QSs increases by one with the addition of each new layer in the island. This causes a reduction of the quantized energy Δ, and a shift of the QS near E_F by $\delta = 2l\Delta/\lambda_F$, where $\lambda_F \approx 3.7l$ ($l = 2.86$ Å is the [111] interlayer spacing of Pb). Around 20 layers, the highest occupied QS is farther away from E_F in strips with even N than that in strips with odd N. This suggests that the former would give rise to lower system energy. The inset of Fig. 4 shows a set of Fermi disks enclosed in the Fermi sphere, representing a quantized free electron system bound by infinite potential barrier. The correction to the surface energy due to the quantization of the electronic contribution is the sum of all the disks minus the equivalent total energy in a continuum case [4]. As N changes from odd to even, the Fermi disks shift down by roughly half of the disk-to-disk separation resulting in a change in surface energy. It has been shown previously that the electron motion is highly anisotropic in the Pb overlayer and $m^*_{\|}/m^*_{\perp} \geq 30$ [19]. In other words, the Fermi surface is quite flat near Γ-L and the equienergy surface in k space becomes highly distorted (the hemisphere of the inset becomes an ellipsoid, long axis along k_z). This increases the occupied states in disks near E_f and enhances the QSE. Photoemission of similar thin metallic films shows that the width of the 2D subband is smaller than the band-to-band separation [20]. Under such a limit, the total electron energy is the sum of a set of occupied flat bands with an equal number of states, except that a filling factor of $1/2$ must be applied to the highest occupied band for the odd N. Figure 4 plots the total quantized electron energy density vs N, which clearly exhibits a *parity effect*, i.e., an oscillatory dependence on odd vs even N. It should be noted that in the real system the barrier at the interface is finite, and the wave function will extend to the vacuum region, giving rise to a surface dipole layer. A density functional calculation based on a uniform ionic background has shown that, while the Friedel oscillation is significantly weakened by the exchange and correlation effect, QSE gives rise to a similar parity effect on the surface potential [21], which is further enhanced by the large anisotropy of the effective mass. QSE also affects charge transfer at the metal semiconductor interface in a similar manner [3]. First principles calculation has shown that the oscillation amplitude of the surface energy for the quantized system is on the order of 10 meV/atom for a free standing film of 20 layer thick [22].

The origin for the sequential strip-flow growth is thus clear. The strip-flow growth on an odd N converts the strip with a higher surface energy to an even N with a lower surface energy. The energy gain becomes smaller as the growth proceeds sequentially from the thinner to the thicker side of the island. When all the strips are in the low energy states (even N), subsequent growth will take place by a double layer strip flow, so as to maintain the low surface energy. This process is much less efficient as it requires at least two atoms arrive in the same place at the same time. In general, once the plateau reaches this low energy phase the surface now becomes difficult to wet,

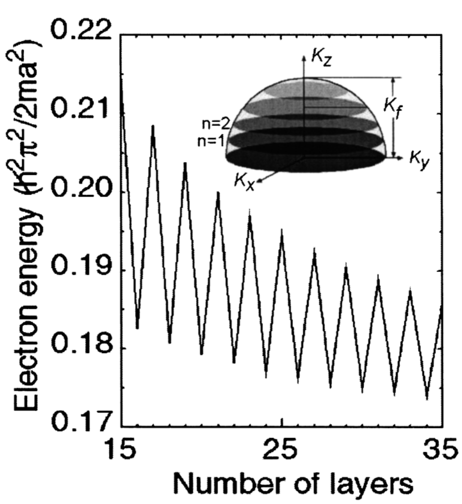

FIG. 4. Electron energy per unit area vs number of layers for a quantized system with $m^*_{\perp} \ll m^*_{\|}$, a being the in plane lattice constant. The inset shows a set of Fermi disks of a free electron system.

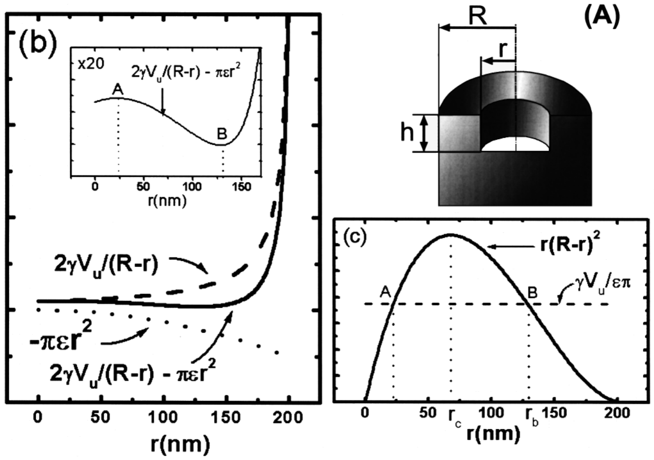

FIG. 5. (a) Model of an ideal ring shaped island. (b) Surface energy of the ring portion of the island with and without QSE (solid vs dashed curve). Inset is a magnified section of the solid curve. (c) Graphical solution to the surface energy minimization [$R = 205$ nm, $V_u = 117\,500$ (nm)^3, $\varepsilon/\gamma = 5\%$].

and it repels the arriving atoms and drives them to the inner wall of the ring. Thus, the ring grows inward while the plateau resists further growth.

To gain more insight into the competing classical and quantum effects, we consider stability of a model ring island depicted in Fig. 5(a) at a given moment during the shape relaxation. Instability arises if the ring decays faster than island relaxation and, hence, we can treat R and H as constant. Since the process is volume preserving, the volume of the ring, $V_u = \pi(R^2 - r^2)h$ is also constant and there is only one independent variable r which characterizes the ring shape. During the initial stage of the ring formation, the change of the elastic energy in the ring portion is considerably smaller than that of the surface energy. Thus, the r-dependent part of the free energy of the ring is $G_C \approx 2\gamma V_u/(R - r)$, plotted in a dashed curve in Fig. 5(b) (per surface tension γ). Under classical consideration, r will decay continuously to zero and a ring-shaped island will become a flattop island as to minimize its surface area. When QSE is taken into account, the new free energy $G_{CQ} = 2\gamma V_u/(R - r) - \pi\varepsilon r^2$, where $\varepsilon > 0$ is the reduction of the surface tension on the plateau inside the ring. The dotted curve plots the correction term and the solid the total surface energy G_{CQ}. The inset of Fig. 5(b) is a magnified portion of G_{CQ}, which clearly reveals a local maximum at point A and a minimum at B, indicating a stable ring island with an inner radius r_b. Setting $\partial G_{CQ}/\partial r = 0$, we find $r(R - r)^2 = V_u\gamma/\pi\varepsilon$. Figure 5(c) gives its graphical solution where we assume $\varepsilon/\gamma = 0.05$, i.e, QSE decreases the surface energy by 5%. If QSE becomes less significant, A and B will move upward and towards each other, and eventually merge into the same point at the threshold value $r_c = R/3$, defined by $\partial[r(R - r)^2]/\partial r = 0$. When $r < r_c$ the ring shape will not be stable. Indeed, we frequently observe a central plateau of roughly $1/3$ the island diameter in small islands, but no stable plateau smaller than this. For larger islands (smaller V_u/R^3) the intersections A and B will move downward, the ring will have a stable and larger opening, which is in good agreement with our observation.

In conclusion, the process that transforms Pb islands from the flattop morphology into the ring shape cannot be explained by either the classical thermodynamics or QSE alone. Rather, it must be accounted for by the competing classical and quantum effects.

*Author to whom correspondence should be addressed. Electronic address: chen@rowland.harvard.edu
†Present address: Physik-Institut, University Zurich, Switzerland.

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