Coulomb Sink: A Novel Coulomb Effect on Coarsening of Metal Nanoclusters on Semiconductor Surfaces

Y. Han, J. Y. Zhu, and Feng Liu
Department of Material Science & Engineering, University of Utah, Salt Lake City, Utah 84112, USA

Shao-Chun Li, Jin-Feng Jia, Yan-Feng Zhang, and Qi-Kun Xue
State Key Laboratory for Surface Physics, Institute of Physics, The Chinese Academy of Sciences, Beijing 100080, China
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We propose the concept of a "Coulomb sink" to elucidate the effect of Coulomb charging on coarsening of metal mesas grown on semiconductor surfaces. We show that a charged mesa, due to its reduced chemical potential, acts as a Coulomb sink and grows at the expense of neighboring neutral mesas. The theory explains qualitatively the most salient features of coarsening of charged Pb mesas on the Si(111) surface, as observed by a scanning tunneling microscope. It provides a potentially useful method for controlled fabrication of metal nanostructures.

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The development of nanoelectronic devices requires controlled fabrication of nanostructures on surface. Two parallel routes have been taken toward this goal: one is the top-down approach, such as nanopatterning, and the other is the bottom-up approach, such as self-assembly. Here, we demonstrate a novel effect of Coulomb charging on coarsening of metal nanoclusters on semiconductor surfaces, which provides a potentially useful method for controlled fabrication of metal nanostructures.

The Coulomb effect is ubiquitous in physics, chemistry, and biology. One well-known manifestation of the Coulomb effect on stability of a cluster is Coulomb explosion. It is defined classically by the Rayleigh instability limit [1], above which an excessively charged cluster becomes unstable and explodes into smaller fragments. For a nanocluster, the critical size for Coulomb explosion depends on the nature of chemical bonding [2].

In this Letter, we demonstrate a novel manifestation of the Coulomb effect on the stability of clusters, the "Coulomb sink." When a metal cluster is charged on a surface it may not explode, but instead grow its size by "sinking" atoms from its neighboring clusters to reduce its Coulomb energy. We elaborate, by both theory and experiment, on the phenomena of Coulomb sink with metal nanomesas grown on semiconductor surfaces. Charging reduces the chemical potential of a charged mesa relative to its neighboring neutral mesas. Consequently, it grows at the expense of its neighbors via a coarsening process. Because one can selectively charge any chosen mesa with a controllable amount of charge, *Coulomb sink provides a unique and effective method for manipulating growth of metal mesas with a size control up to millions of atoms.*

The growth of metal film on semiconductor substrates proceeds via Volmer-Weber mode [3,4], forming three-dimensional islands, when the surface energy of the film is much higher than that of the substrate. The islands may adopt an equilibrium mesa shape defined by surface-energy anisotropy, such as Au mesas on C(0001) [5] and Pb mesas on the Si(111) surface [6,7]. For simplicity, we assume they have a cylindrical shape of radius R and height h, as shown in Fig. 1. The energy of a neutral mesa, in reference to a bare surface, is then

$$E = (\pi R^2)(\gamma_{\mathrm{mt}} + \gamma_i - \gamma_s) + (2\pi Rh)\gamma_{\mathrm{ms}}, \qquad (1)$$

where γ_{mt} and γ_{ms} are, respectively, the surface energy of the mesa top and the mesa sidewall, and γ_i and γ_s are, respectively, mesa-substrate interface energy and substrate surface energy.

During postgrowth, an array of mesas undergoes coarsening, with larger mesas growing at the expense of smaller ones. However, coarsening slows down as the average mesa size increases [8]. In particular, after mesas attain their equilibrium shape, coarsening may be prohibited by the existence of an energy barrier for nucleating new layers on the mesa top [6,9].

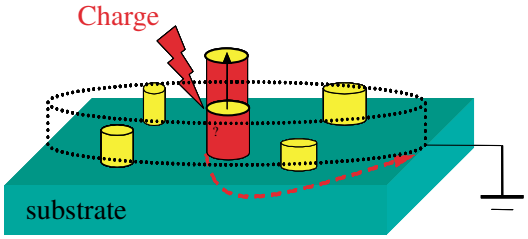

FIG. 1 (color online). Schematic illustration of a cylindrical capacitor formed by a charged metal mesa (dark/red) and the distant groundings (the dotted lines). The dashed arrow line indicates the discharging process: the pink of the cylinder indicates the height growth of the charged mesa.

Now, consider one chosen mesa is charged by Q, using a scanning tunneling microscope (STM), and the charge will subsequently discharge to the substrate within a period of time, as illustrated in Fig. 1. By considering a capacitor formed between the charged mesa and its surroundings, its energy is instantaneously increased by $E = Q^2/(2C)$, where C is the capacitance.

The capacitance of a conductor is proportional to its size, D. Thus to lower its Coulomb energy, $E \sim 1/D$, the charged mesa (cluster in general) may increase its size, so as to maximize its capacitance. For coarsening, this implies that the chemical potential of the charged cluster is instantaneously reduced by $\mu \sim dE/dD \sim -1/D^2$, with respect to its neighboring uncharged clusters, so it grows at the expense of its neighbors.

Specific to mesa geometry, we model the charging effect by a coaxial cylindrical capacitor of height h, as shown in Fig. 1. The inner conductor is the charged mesa having a radius R with charge Q; the outer conducting shell (dotted lines) represents the distant groundings, having a much larger radius R_g. Its capacitance is calculated as [10] $C = \frac{2\pi\varepsilon}{\ln(R_g/R)}h$, where ε is the dielectric constant. So, the excessive Coulomb energy of the charged mesa is $E = \frac{\ln(R_g/R)}{4\pi\varepsilon}\frac{Q^2}{h}$.

An increase of either h or R results in a decrease of E. To specify the growth of height versus radius, we define a "partial" chemical potential for height growth, μ_h, representing the change of Coulomb energy with respect to changing height at a fixed radius as

$$\mu_h = \Omega \frac{dE}{dV}\bigg|_{R=\text{const}} = -\Omega \frac{\ln(R_g/R)}{4\pi^2\varepsilon R^2}\frac{Q^2}{h^2}, \qquad (2)$$

where Ω is the atomic volume, and a partial chemical potential for radius growth, μ_R, representing the change of Coulomb energy with respect to changing radius at fixed height, as

$$\mu_R = \Omega \frac{dE}{dV}\bigg|_{h=\text{const}} = -\Omega \frac{1}{8\pi^2\varepsilon R^2}\frac{Q^2}{h^2}. \qquad (3)$$

A growth index function can then be defined as

$$S_\mu = \mu_h - \mu_R = -\frac{\Omega}{8\pi^2\varepsilon R^2}\frac{Q^2}{h^2}\left(2\ln\frac{R_g}{R} - 1\right), \qquad (4)$$

which tells the energetically favored growth direction. Because $R_g \gg R$, $S_\mu < 0$. It is readily seen that the charged mesa always favors growth in height.

Charging affects coarsening by breaking down the chemical-potential balance between the original neutral mesas, as the potential of the charged mesa is decreased by an amount $\sim Q^2$. It makes the charged mesa act effectively as a Coulomb sink to attract atoms from the surrounding neutral mesas. Therefore, it triggers the otherwise "ceased" coarsening process by creating a high supersaturation around the charge mesa to overcome the energy barrier for nucleating new layers [6,7] to grow in height.

To assess the amount of growth induced by charging, we consider the coarsening process to be controlled by the attachment of adatoms to the mesa [11]. Its rate of height growth can then be expressed as

$$\frac{dh}{dt} = -\frac{C_{\text{AD}}}{\pi R^2}(\mu - \overline{\mu}) \approx -\frac{C_{\text{AD}}}{\pi R^2}\mu_h, \qquad (5)$$

where C_{AD} is a coefficient related to the adatom attachment rate and the atomic volume. μ is the chemical potential of the charged mesa, and $\overline{\mu}$ is the mean chemical potential of the surrounding neutral mesas.

In the cylindrical-capacitor model, we assume charge being distributed on the mesa sidewall. This indicates that the height growth starts along the mesa edges, creating many steps. Consequently, the charged mesa continues to grow even after discharging, since coarsening can now proceed via step flow without the need of nucleating new layers. (The time of discharging will be discussed later.) The growth after discharging is much slower, as it is driven by a smaller chemical-potential difference due to mesa size difference and by the tendency for the growing mesa to eliminate steps to resume the flat-top equilibrium shape. The growth stops until a flat top is formed. Further growth can be triggered again only by another charging pulse.

For a mesa with a flat top sitting on a vicinal surface, its partial height-growth potential is lower on the thinner left edge than that on the thicker right edge; i.e., $\mu_h^L < \mu_h^R$ as shown in the middle mesa in Fig. 2, because the potential is negative and scales inversely with height [Eq. (2)]. If charge distributes uniformly around its sidewall, the charged mesa will grow first its left edge (lower potential) and then its right edge. Later, after discharging, growth continues toward the center from the sides, eliminating steps created by charging to resume a flat top. This growth sequence is illustrated on the middle mesa in Fig. 2 as steps 1, 2, and 3.

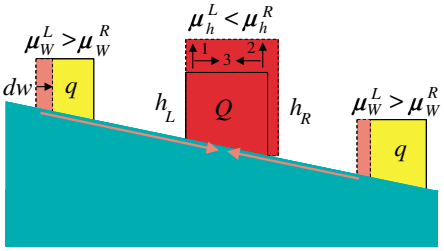

FIG. 2 (color online). Illustration of growth of a charged (Q) mesa and dissolution of two neighboring less charged (q) mesas on a vicinal surface. The middle mesa grows its height in steps 1, 2, and 3, as $\mu_h^L < \mu_h^R$. Both neighboring mesas dissolve their left edge as $\mu_w^L > \mu_w^R$. The middle mesa may also grow its width on the right as $\mu_w^L > \mu_w^R$.

The charging triggered coarsening process and the growth sequence predicted above have been confirmed by the coarsening of Pb mesas on Si(111) under STM charging. The experiment was performed on an OMICRON UHV molecular beam expitaxy-STM system. About 3 monolayers Pb was deposited on the clean Si(111)-(7 × 7) surface at ~150 K, forming flat-top mesas. The charging was applied at room temperature by an pulse of 10 V and a tunneling current 20 pA with feedback on for about several ms. Right after the pulse, normal room temperature STM scanning (1.5 V and 20 pA) was resumed to monitor the morphology evolution.

Without charging, the mesas remain unchanged for days at room temperature, in agreement with previous observation [6]. Figure 3 shows the charging-induced growth of a giant Pb mesa. Because the mesa forms initially with a flat top (the $t \leq 0$ line scan in Fig. 3) on a vicinal surface having a staircase of steps, it has a wedge shape, covering seven Si steps with its left edge being thinner than its right edge.

Notice that about 40% of the total growth is done within the first line scan after charging ($\sim 10^{-4}$ min). This indicates that a massive growth in height at the edge has occurred within the charging-discharging time, which could be even shorter than 10^{-4} min. After discharging, the growth continues via step flow, mediated by the steps created by the initial edge-height growth. Obviously, the growth after discharging is much slower and stops until the mesa resumes a flat top at 51'. The final mesa height is then uniquely defined by the maximum initial height growth at the edge. Furthermore, although the STM charging tip is placed on the right foot of the mesa, the initial height growth starts on the thinner left edge and the height growth on its left edge is more substantial than on its right edge. All these observations are consistent with theory.

For simplicity the theory uses a perfect cylindrical shape with uniform charge distribution. In experiment, the mesa has a distorted hexagonal shape. Figure 3 shows that the growth favors at the corners of the mesa. This possibly indicates that charge is not uniformly distributed around the mesa but concentrated on corners where sidewall curvature is larger.

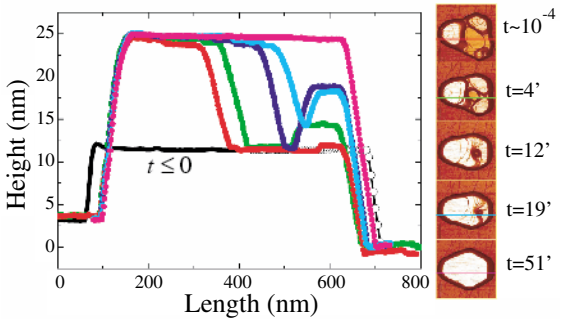

FIG. 3 (color online). Growth sequence of a Pb mesa on a vicinal Si(111) surface. The right panel shows sequential STM images of the mesa recorded at different times (in min). The left graph shows line scans of the mesa height as marked in the images. The charging STM top is placed on the right foot of the mesa. The image size is 800 nm × 800 nm.

One unknown parameter in the Coulomb sink model is how long the charge stays on the mesa, which we are unable to determine from the experiment. Theoretically, the charge might be assumed to decrease with time following a capacitor-resistor circuit $Q(t) = Q_0 e^{-t/\tau}$, where Q_0 is the charge at $t = 0$ and τ is the discharging time constant. Substituting $Q(t)$ into Eqs. (2) and (5), we obtain the height growth as $h = \beta \tau^{1/3} Q_0^{2/3}$, with $\beta^3 = [3\Omega C_{\mathrm{AD}} \ln(R_g/R)]/(8\pi^2 \varepsilon R^4)$. In terms of atoms, the growth is $N \sim (\beta \pi R^2/\Omega)\tau^{1/3} Q_0^{2/3}$.

So, the amount of growth scales with τ in a 1/3 power law and with Q_0 in a 2/3 power law. We note that although τ could be very short, the growth within the time of discharging may still be substantial if Q_0 is large. Using the typical data of Pb and Si (doping level of $\sim 10^{17}$ cm^{-3} for our sample), we roughly estimate that the interface capacitor is $C_i \sim 10^{-16}$–10^{-14} F [12,13] and the interface resistance is $R_i \sim 10^8\ \Omega$ [14], which gives $\tau \sim 10^{-8}$–10^{-6} s. Using $\Omega_{\mathrm{Pb}} = 0.03$ nm^3 and $C_{\mathrm{AD}} \sim 10^{-3}$–$10^{-5}$ m^3 J^{-1} s^{-1}, we estimate that a Pb mesa on Si(111) with a radius of 100 nm may "sink" ~1–10 atoms within the discharging time if it is charged with one electron. Roughly speaking, if a mesa is charged with 10^6 electrons, it may sink up to 10^6 atoms, as observed in experiments (see the massive amount of growth within 10^{-4} min in Fig. 3).

We stress that the crude estimation we provide here is only to demonstrate the quantitative feasibility of the Coulomb sink model. We have also done some experiments using different bias voltages for charging while keeping other parameters fixed; the amount of growth does increase with increasing voltage. Unfortunately, we are unable to quantitatively confirm the theoretical prediction that the amount of the charging-induced growth scales with charge in a 2/3 power law, because we cannot accurately determine the amount of charge and the amount of growth before discharging.

The charged mesa grows at the expense of its neighboring mesas. Next, we show that charging can also influence the dissolution of the neighboring mesas if they are also charged but with much less amount of charge $q \ll Q$. If so, they will always lose their atoms from the thinner left edge independent of their location, as illustrated in Fig. 2. To demonstrate this point, we define another partial chemical potential, μ_w, representing the change of Coulomb energy with respect to changing width (w) at fixed height (h) as

$$\mu_w = \Omega \frac{dE}{dV}\bigg|_{h=\mathrm{const}} = \Omega \frac{\ln(R_g/R)}{4\pi\varepsilon(dw)^2} \frac{q^2}{h^2}. \qquad (6)$$

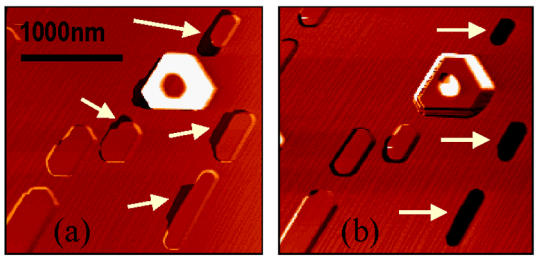

FIG. 4 (color online). (a) Difference STM image taken before and after one charging pulse at a time interval of 1.5 h, illustrating the growth of middle mesa (white) and dissolution of left edges of its neighbors (black regions pointed by arrows). (b) Difference STM image taken before and after another charging pulse at a time interval of 15 h, illustrating the complete dissolution of three neighbors.

The partial chemical potential for width dissolution (or width growth) is higher on the left side than on the right side, i.e., $\mu_w^L > \mu_w^R$, as shown on the two outside mesas in Fig. 2, because μ_w is positive and scales inversely with height. If charge distributes uniformly around the mesas' sidewall, they will always dissolve their higher-potential left sides, independent of their locations. For the same reason, if the middle mesa grows also somewhat its width (much less than its height growth), it will expand the right side, the thicker edge of lower chemical potential, as observed in Fig. 3.

The dissolution of neighboring mesas has indeed been observed in experiments. Figure 4(a) shows the difference of two STM images taken with a time interval of $\sim$1.5 h, before and after one 10 V pulse (20 pA) being applied to the middle mesa. Clearly, the charged mesa grows (appearing white), while its neighbors shrink (black regions pointed by the arrows).

In parallel to the growth of the middle mesa, the dissolution of the neighboring mesas undergoes two stages: the first stage of fast dissolution within discharging time followed by the second stage of slow dissolution after discharging. Figure 4 shows that the neighboring islands dissolve always their left thinner edges, especially their "left-side" corners, no matter where they locate. In the first stage if they are charged, this can be caused by charge being concentrated at and discharged from the corners. In the second stage when they are neutral, the strain effect would favor dissolution from their thinner edge where the strain is higher, while the curvature effect would favor dissolution from convex corners where the surface energy is higher. Also, the middle mesa shifts slightly to the right, because of dissolution of its left edge and expansion of its right edge, governed by similar physical mechanisms. Effectively, the middle mesa moves by a chemical-potential gradient within the mesa via intramesa diffusion. Similar motion and mechanisms have been shown in coarsening of strained islands [11]. If another charging pulse is applied, some smaller neighboring mesas dissolve completely into the growing charged mesa, as shown in Fig. 4(b).

In conclusion, we demonstrate a new concept of Coulomb sink to elucidate coarsening of metal mesas on a semiconductor surface under STM charging. Charging reduces the chemical potential of the charged mesa, making it act as a Coulomb sink to grow at the expense of its neighboring mesas. Thus, it triggers an otherwise ceased coarsening process. By introducing a partial chemical potential for the growth of height versus radius, we show that the charged mesa grows preferentially its height and the growth proceeds first rapidly by nucleation of new layers around the island edge creating many steps, and then continues slowly via step flow after discharging to resume a flat top. The theory has successfully explained most salient qualitative features observed in the coarsening of charged Pb mesas on Si(111). Also, the theory predicts that the initial growth before discharging scales with the amount of charge in a $2/3$ power law, which remains to be confirmed experimentally.

Coulomb sink, leading to cluster agglomeration, is effectively a reversed process of Coulomb explosion, leading to cluster fragmentation. It provides a unique and effective method for manipulating growth of metal nanoclusters on semiconductor or insulator surfaces with a size control up to millions of atoms.

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