

Self-Assembly of Three-Dimensional Metal Islands: Nonstrained versus Strained Islands

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A theoretical model for the Volmer-Weber growth of three-dimensional metal islands is proposed, with a dipolar island edge-edge interaction. The existence of such an island edge effect makes the island shape dependent on island size. Furthermore, it induces a stable island size against coarsening, leading to self-assembled islands of uniform size. The dependence of the stable island size on total film coverage is shown to be different for nonstrained versus strained islands, in the regime of strong island-island interaction.

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The epitaxial growth of three-dimensional (3D) islands is of both scientific interest and technological importance. The surprising size uniformity of 3D islands achieved in the growth of both elemental and compound semiconductor thin films [1–6] has shown great promise for their use as quantum dots. The experiments stimulated extensive theoretical studies, which have progressively advanced our understanding of the epitaxial growth of 3D islands. In particular, various strain-induced thermodynamic and kinetic mechanisms [1,3,6–12] have been proposed for self-assembly and self-organization of 3D semiconductor islands.

In contrast to *semiconductor*, the size uniformity of 3D *metal* islands is less common [13–20] and little theory has been reported for self-assembly of 3D metal islands. Recently, in some systems, such as Au [21] and Pd [22] on the TiO₂ surface and Fe on the NaCl(001) surface [23], very good size uniformity has also been achieved for 3D metal islands. However, the physical origin of such size uniformity has yet to be explored. Here, I propose a theoretical model for self-assembly of 3D metal islands in the Volmer-Weber (VW) growth mode, which leads to uniform island size distribution.

The growth and coarsening of 3D metal islands are investigated with a thermodynamic model that includes an island edge effect. Its existence makes the island shape (surface contact angle) change continuously with island size. Also, it induces a stable island size against coarsening, leading to self-assembly of islands with uniform size. In the regime of strong island-island interaction, the stable island size depends on the total coverage of the film. This dependence is rather different for nonstrained vs strained islands, allowing us to distinguish the two cases.

The growth of metal thin film on insulator substrate often proceeds in the VW mode, i.e., the 3D island growth, because the surface energy of the metal film is much higher than that of the substrate [13]. We consider the metal island to be either nonstrained or strained. For the nonstrained island, we assume a perfect lattice match between metal island and substrate (or nearly perfect so

that misfit strain is negligible). But there exists still a large island edge effect arising from the different intrinsic surface stress of metal and substrate. For the strained island, we assume it remains coherent without dislocations. The misfit strain is expected to further enhance the edge effect, in addition to bulk strain energy.

In terms of self-assembly, we point out several major differences between 3D metal and semiconductor islands. First, the metal islands are usually nonfaceted (or multifaceted), adopting a spherical-cap shape due to isotropic surface energies, while the semiconductor islands are usually faceted, adopting a pyramidal shape due to anisotropic surface energies. Consequently, the metal islands can change their shape (contact angle) continuously while the semiconductor islands have to retain their shape or change their shape abruptly from one facet angle to another. The abrupt shape change provides a self-assembly mechanism for semiconductor islands [3], which is absent for metal islands. Second, the epitaxial relation between the metal island and substrate is sometimes unclear [24], making it difficult to determine the amount of strain in the metal islands. In contrast, the semiconductor islands grow on the substrate of the same crystal structure with well-defined misfit strain. In fact, most self-assembly and self-organization mechanisms proposed so far for semiconductor islands are based on strain effects [1,3,6–12]. Third, the metal islands grow via the VW mode, without a wetting layer, while the semiconductor islands usually grow via the Stranski-Krastanow mode, in which the wetting layer may affect self-assembly [9].

We first determine the optimal shape of a nonstrained metal island at the early stage of growth when islands are too far apart for ripening to take place. The island, nucleating and growing in the shape of a spherical cap, is defined by two parameters, the contact angle, θ , and the radius of island base, R , as shown in Fig. 1. The surface energies include

$$E_s = \pi R^2(\gamma_i - \gamma_s) + 2\pi R^2(1 + \cos\theta)^{-1}\gamma_m, \quad (1)$$

where γ_m , γ_s , and γ_i are, respectively, surface energy of

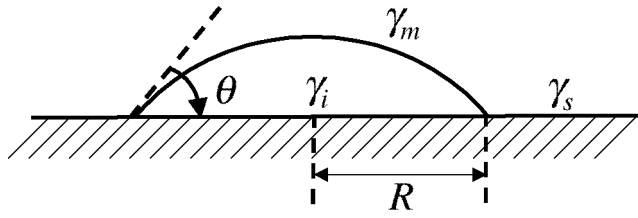


FIG. 1. Schematics of a 3D metal island, showing the cross section of a spherical cap. θ is the contact angle; R is the radius of the circular island base.

island, of substrate, and island-substrate interface energy. Minimization of E_s leads to a constant contact angle given by $\cos\theta_0 = (\gamma_s - \gamma_i)/\gamma_m$, independent of island volume.

However, even for a nonstrained island, additional energies associated with island edge are expected. In general, there is a local island edge energy, γ_b , analogous to surface step energy. Also, the intrinsic surface stress of metal island generally differs from that of the substrate. The stress discontinuity along the island edge introduces a negative elastic relaxation energy. The total island edge energies can be calculated as [25,26]

$$E_e = 2\pi R\gamma_b - 2\pi R\gamma_d \ln \frac{R}{a}, \quad (2)$$

where γ_d represents elastic energy per unit length of island edge [27]. $a = a_0 e^2/4$ and a_0 is a cutoff length representing the width of the island edge.

More generally, we may model the surface with a two-phase domain structure [25]. Then, the island edge energies represent a local domain boundary energy (γ_b) and a dipolar domain interaction energy ($\propto \gamma_d$). It is important to realize that the physical origin of the dipolar interaction can be elastic due to surface stress difference, or it can be electrostatic or magnetostatic for metal and magnetic islands. Such edge effects are present for both nonstrained and strained islands.

Minimization of island total energy ($E_s + E_e$) gives

$$\cos\theta = \cos\theta_0 - \frac{\gamma_b}{\gamma_m R} + \left(\frac{\gamma_d}{\gamma_m R}\right) \ln \frac{R}{a}. \quad (3)$$

Thus, the island contact angle, θ , is no longer constant but depends on island size. To illustrate the general trend, Fig. 2 shows the functions of θ vs R for different ratios of γ_d/γ_m with $\theta_0 = 60^\circ$, $\gamma_b/\gamma_m = 1.0$, and $a_0 = 1.5 \text{ \AA}$. Clearly, the edge effect drives the island contact angle increase continuously with increasing island size.

We next consider the coarsening of nonstrained islands at the later stage of growth, governed by chemical potential. At the dilute limit, we neglect the island-island interaction. Assuming sufficient diffusion for islands to always attain their optimal shape during coarsening, i.e., kinetically they change their shape much faster than change their size, then the total energy of an island with

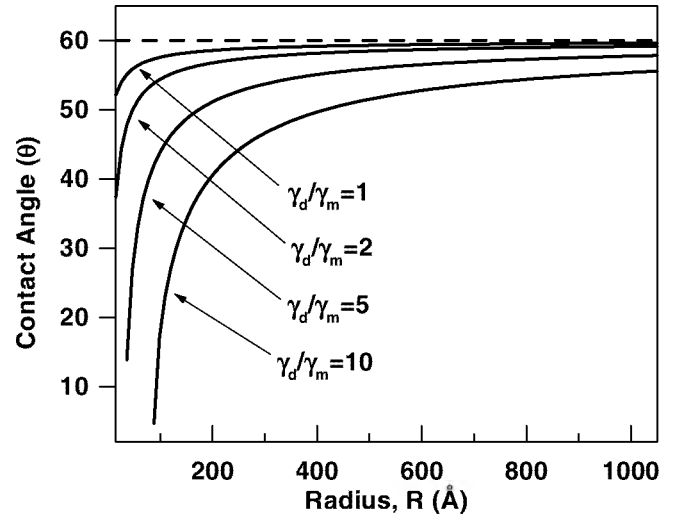


FIG. 2. The island contact angle (θ) vs island base radius (R) for different island edge and surface energy ratios of γ_d/γ_m , with other parameters set at $\theta_0 = 60^\circ$, $\gamma_b/\gamma_m = 1.0$, and $a_0 = 1.5 \text{ \AA}$.

base radius R of optimal contact angle θ is

$$E_t = 3R^2 \left(\frac{f(\theta)}{\sin^2\theta} \right) \gamma_m + \pi R\gamma_b - \pi R\gamma_d \ln \frac{R}{ea}, \quad (4)$$

where $f(\theta) = \frac{\pi}{3}(2 - 3\cos\theta + \cos^3\theta)$. The island chemical potential is

$$\mu = v \frac{dE_t}{dV} = v \left[\frac{A\gamma_m}{R} + \frac{B\gamma_b}{R^2} - \frac{B\gamma_d}{R^2} \ln \frac{R}{a} \right], \quad (5)$$

where v is the atomic volume, $A = 2\sin\theta$, and $B = \frac{\pi}{3}f^{-1}(\theta)\sin^3\theta$. Without the ‘‘surface-energy’’ term, the last two ‘‘edge-energy’’ terms in Eq. (5), similar to 2D islands [26], lead always to a minimum potential of $\mu_0 = -\frac{1}{2}vB\gamma_d R_0^{-2}$ at $R_0 = a \exp(\frac{\gamma_b}{\gamma_d} + \frac{1}{2})$. However, whether a 3D island can still have a size of minimum potential depends on the ratio of surface energy over edge energy. We write the reduced chemical potential in terms of μ_0 and radius in R_0 ,

$$\frac{\mu}{\mu_0} = \alpha \left(\frac{R}{R_0} \right)^{-1} - 2 \left(\frac{R}{R_0} \right)^{-2} \ln \frac{e^{1/2} R}{R_0}, \quad (6)$$

where $\alpha = \frac{2AR_0\gamma_m}{B\gamma_d}$. Similar to a strained faceted semiconductor island [8], the metal island exhibits a stable (or metastable) size against coarsening for $\alpha < 1.0$. Thus, the 3D metal islands will self-assemble with uniform size when their edge energy dominates over surface energy.

At the dense limit, island-island interaction becomes significant, which will change the size of stable islands. The interaction energy, arising from the edge effect, between two nonstrained islands of radius R separated by D can be calculated [26] as $E_{ie} = \pi^2 \gamma_d \frac{R^2}{D^3}$. It further modifies the optimal island shape by adding a term, $-2\pi R^2 \gamma_d \gamma_m^{-1} D^{-3}$ to Eq. (3). Thus, the total energy of

an island maintaining the optimal shape becomes

$$E_t = 3R^2 \left(\frac{f(\theta)}{\sin^2 \theta} \right) \gamma_m + \pi R \gamma_b - \pi R \gamma_d \ln \frac{R}{a} - \pi^2 \gamma_d \frac{R^4}{D^3}. \quad (7)$$

For a dense array of islands of equal volume (V) with a number density of n , the total film coverage is $\Theta = nV$. Approximately, $D^2 = 1/n$ [26]. Then, the reduced island chemical potential becomes

$$\frac{\mu}{\mu_o} = \alpha \left(\frac{R}{R_0} \right)^{-1} - 2 \left(\frac{R}{R_0} \right)^{-2} \ln \frac{e^{1/2} R}{R_0} + \beta \left(\frac{R}{R_0} \right)^{-7/2} \Theta^{3/2}, \quad (8)$$

where $\beta = \frac{2CR_0^{-3/2}}{B}$ and $C = \frac{1}{6} \pi^2 (\sin \theta)^{15/2} f^{-5/2}(\theta)$.

A phase diagram can be constructed in the parameter space of α and β to define the regime in which islands are stable against coarsening [8]. Here, we focus on the dependence of stable island size on total coverage inside the stable regime. In Fig. 3, using $\alpha = 0.1$ and $\beta = 0.1$, we plot μ/μ_o vs R/R_0 for different coverage of $\Theta = 1 \rightarrow 5$. The stable size (R_{\min}) of nonstrained islands increases almost linearly with increasing coverage.

Now, we analyze how the edge effect influences the growth and stability of strained islands. The misfit strain contributes a bulk energy term, $E_b = \gamma_E S(R, \theta) V$, where γ_E is the strain energy per unit volume; $S(R, \theta)$ is a shape factor that cannot be solved analytically. Numerical simulations [28,29] have shown that the contact angle of the strained island, in the *absence* of the edge effect, increases monotonically with increasing island size.

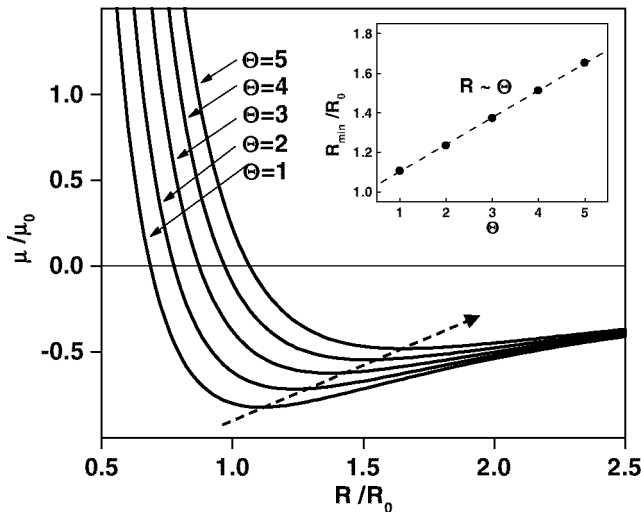


FIG. 3. The reduced chemical potential vs the reduced island size (the radius of island base) at five different total coverages for nonstrained island. The dashed line arrow indicates the shifting of the radius of minimum chemical potential (R_{\min}) with increasing coverage (Θ). The inset shows R_{\min} as a function of Θ and a linear fit (dashed line) to the data (solid dots).

Here, we show that the *presence* of the edge effect also makes the contact angle increase. Therefore, the contact angle of both nonstrained and strained island increases with increasing size but the increase is faster for the strained island.

It has indeed been observed that the contact angle of Au [21], Pd [22], and Fe [23] islands increases with increasing island size, indicating these islands are influenced by edge and/or strain effects. However, we cannot determine which effect (edge or strain) is the dominating factor, because it is difficult to know the exact form of the dependence of island shape on island size from the limited data available and the difference between the nonstrained and strained island is only quantitative. A better way to distinguish the nonstrained from strained islands is by measurement of self-assembled island size vs film coverage, as they are qualitatively different.

In the *absence* of the edge effect, strained islands will not be stable against coarsening, even taking into account the misfit strain-induced island-island interaction [28,29]. However, when the *presence* of the edge effect introduces the stability, the strain-induced island-island interaction will influence the size of stable islands and hence its dependence on film coverage. The interaction can be calculated as $E_{ib} = K \gamma_E \frac{V^2}{D^2}$ [8], where K is a constant, which adds to the island chemical potential,

$$\frac{\mu}{\mu_o} = \alpha \left(\frac{R}{R_0} \right)^{-1} - 2 \left(\frac{R}{R_0} \right)^{-2} \ln \frac{e^{1/2} R}{R_0} + \beta \left(\frac{R}{R_0} \right)^{-7/2} \Theta^{3/2} + \delta \left(\frac{R}{R_0} \right)^{-3/2} \Theta^{3/2}, \quad (9)$$

where $\delta = [K \gamma_E f^{-1/2}(\theta) \sin^3 \theta R_0^{1/2}] / (B \gamma_d)$. In Fig. 4,

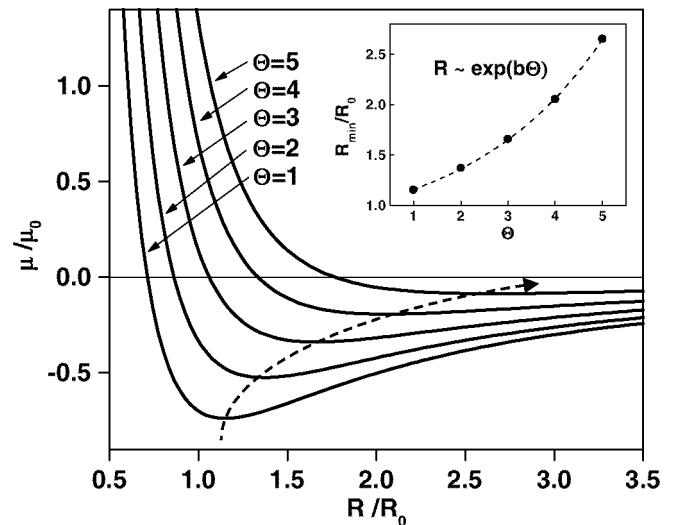


FIG. 4. The reduced chemical potential vs the reduced island size at five different total coverages for a strained island. The notations are the same as in Fig. 3, except the exponential dependence of R_{\min} on Θ .

using $\alpha = 0.1$ and $\beta = 0.1$ as in Fig. 3, plus $\delta = 0.1$, we plot μ/μ_0 vs R/R_0 for coverage, $\Theta = 1 \rightarrow 5$. The stable size (R_{\min}) of strained islands increases approximately exponentially with increasing coverage.

Thus, the dependence of stable island size on film coverage is different for nonstrained vs strained islands: the former increases linearly with increasing coverage while the latter exponentially. Measurement of such dependence will then allow us to distinguish the two cases. The increase of island base radius with increasing coverage has been observed for Fe islands on NaCl(001) [23]. Qualitatively, such behavior is also expected for faceted strained islands.

In conclusion, a theoretical model is proposed for self-assembly of 3D metal islands. We show that different from the faceted semiconductor islands, the surface contact angle of even nonstrained metal islands increases continuously with increasing island size, if an island edge effect is present. The contact angle of the strained metal islands increases even faster with increasing size, because misfit strain may enhance the edge effect and strain relaxation alone also makes the contact angle increase. Furthermore, the edge effect induces a stable island size against coarsening. In the regime of strong island-island interaction, the dependence of stable island size on film coverage is almost linear for nonstrained islands but approximately exponential for strained islands. This difference allows us to effectively determine whether the island-island interaction is dominated by the edge or strain effect.

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