

Metastability of Ultradense Arrays of Quantum Dots

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We present a linear stability analysis of ultradense arrays of coherently strained islands against Ostwald ripening. Surprisingly, short-range elastic interactions are found to overcome the destabilizing contribution of surface energy, leading to a metastable array of quantum dots. Simulations of Ostwald ripening kinetics directly verify the existence of this metastable regime and confirm the nature of the most unstable mode for subcritical island coverage.

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Self-assembly and self-organization of strained three-dimensional (3D) islands during heteroepitaxial growth provides an attractive route to the nanofabrication of quantum dot (QD) arrays. A prerequisite for the employment of these islands as QDs is that they possess a narrow size distribution [1,2]. Consequently, a full understanding of the factors governing the energetics and stability of uniformly sized island arrays is of both scientific and technological significance [3–5]. In particular, it is important to identify the most basic thermodynamic ingredients which are necessary for stability.

The growth of 3D clusters on surfaces has been extensively studied for unstrained systems [6]. Of particular relevance to the formation of uniformly sized dots is the late stage growth regime where the whole cluster distribution interacts with a supersaturation only slightly in excess of the average-sized island chemical potential [6,7]. Under these conditions, the cluster size distribution evolves according to well-known models of Ostwald ripening and no stable (or metastable) configurations are obtained [8,9].

In 3D systems subjected to misfit strain, the situation is more complex. It has been shown that surface-stress induced force monopoles at island edges can facilitate island size uniformity [10–12]. This is equivalent to a strain-renormalized surface energy which can be *negative* and stabilize 3D island arrays. However, if a positive island surface energy is assumed, it is generally accepted that no stable or metastable configurations exist [13,14]. In particular, treated in a mean-field approximation, elastic interactions increase the array total energy, accelerate the ripening kinetics [15], and are regarded as destabilizing [4,10,11].

In this Letter, we focus on the stability and ripening dynamics of an arbitrarily dense array of 3D islands of *positive* surface energy during annealing. By treating the near-field elastic interaction *exactly*, we identify a previously unknown metastable regime in which densely packed arrays are stable against small fluctuations. We show that, whereas the long-range dipole-dipole part of

the elastic interaction between islands destabilizes an array of islands, favoring ripening, the short-range part of the interaction produces a stabilizing effect. For very dense arrays, this stabilizing effect overcomes the driving force to reduce the island surface energy via ripening, and the system is stable against the exchange of a small amount of material between islands. Thus, a dense array of 3D islands is metastable due solely to short-range elastic interactions between islands.

To make the system tractable, we assume that all islands, which may differ in volume, have an identical conical shape with a small tilt angle $\theta \ll \pi/4$. Such a shape accurately mimics the form of real QDs and greatly simplifies the consideration of the elastic interaction due to angular symmetry. The total energy change of the system due to formation of islands is a sum of the surface and strain energy, $E_{\text{total}} = \Delta E_{\text{surf}} + \Delta E_{\text{elast}}$, the effects of surface stress being neglected. For a conical island,

$$\Delta E_{\text{surf}} = \pi \rho^2 [\gamma(\theta) \sec \theta - \gamma(0)] = \frac{3}{2} \beta V^{2/3}, \quad (1)$$

where ρ is the radius of the island base, V is the island volume, and $\gamma(\theta)$ and $\gamma(0)$ are the surface energies of the tilted surface of the island and of the flat surface of the wetting layer, respectively, with $\beta = 2\pi^{1/3} 3^{-1/3} (\cot \theta)^{2/3} [\gamma(\theta) \sec \theta - \gamma(0)]$. We consider a typical case where $\beta > 0$, thus the islands, without elastic interaction, would tend to ripen to reduce the overall surface energy.

For a system having a shallow surface profile $z = h(\mathbf{r})$ such that $|\nabla h| \ll 1$, the elastic energy can be written in an explicit form [13]

$$\Delta E_{\text{elast}} = -\frac{1}{2} \int d^2 \mathbf{r} d^2 \mathbf{r}' f_i(\mathbf{r}) \chi_{ij}(\mathbf{r} - \mathbf{r}') f_j(\mathbf{r}'), \quad (2)$$

where \mathbf{r} and \mathbf{r}' are 2D position vectors, χ is the elastic Green's function of the surface which describes the elastic response to an applied force, and $f_i = \nabla_j \sigma_{ij}$ is the force density at the surface. Here, $\sigma_{ij} = \sigma_b h(\mathbf{r}) \delta_{ij}$ is the 2D island stress tensor, where σ_b is the xx or yy component of

the bulk stress of a uniform flat film of the deposited material coherently strained to the substrate and allowed to relax in z , and $h(\mathbf{r})$ is the height (thickness) of the island at position \mathbf{r} .

We solve Eq. (2) using the surface Green's function χ of an isotropic solid [16], giving

$$\Delta E_{\text{elast}} = -\alpha J \tan\theta \sum_a V_a + \frac{\alpha}{2\pi} \sum_a \sum_{b \neq a} \frac{V_a V_b}{R_{ab}^3} F\left(\frac{\rho_a}{R_{ab}}, \frac{\rho_b}{R_{ab}}\right). \quad (3)$$

Here, the first term is the energy of self-relaxation of the islands, and the second term is the interaction energy. The coefficient $\alpha = (1 + \nu)(1 - \nu)^{-1} Y \varepsilon_0^2$, where ε_0 is the lattice mismatch between the deposit and the substrate, Y and ν are the Young's modulus and the Poisson's ratio assumed to be equal in both materials, and R_{ab} is the distance between centers of the bases of two islands. The coefficient $J = 1.059$ in Eq. (3). The correction factor F is the deviation of the exact interaction energy from the dipole-dipole approximation. It equals

$$F(\eta_1, \eta_2) = \sum_{s=0}^{\infty} \left\{ \sum_{p=0}^s \left[\frac{\eta_1^p \eta_2^{s-p}}{\Gamma(p+1)\Gamma(s-p+1)} \right]^2 \times \frac{9}{4(p+1)(p+\frac{3}{2})(s-p+1)(s-p+\frac{3}{2})} \right\} \times \left[\frac{\Gamma(\frac{3}{2}+s)}{\Gamma(\frac{3}{2})} \right]^2. \quad (4)$$

For remote islands, when $\eta_{1,2} \rightarrow 0$, the correction factor

$$\Lambda(\mathbf{k}) = \xi \Omega \frac{1}{k_B T} V_0^{1/3} \left[\frac{1}{3} \beta V_0^{-4/3} - \frac{\alpha}{2\pi} \sum_b \exp(-i\mathbf{k} \cdot \mathbf{R}_{ab}) \frac{\partial^2}{\partial V_a \partial V_b} \left[\sum_c \sum_{d \neq c} \frac{V_c V_d}{R_{cd}^3} F\left(\frac{\rho_c}{R_{cd}}, \frac{\rho_d}{R_{cd}}\right) \right] \right]. \quad (7)$$

Parameters characterizing an array of cones are the surface coverage q , and the average cone volume V_0 . It is convenient to express the volume V_0 in terms of the critical volume V_{cr} for the nucleation of a single isolated island, which is defined from the balance of the surface energy and the energy of self-relaxation, $d/dV[(3/2)\beta V^{2/3} - J\alpha \tan\theta V] = 0$, hence, $V_{\text{cr}} = (J\alpha \tan\theta/\beta)^{-3}$. Then, Eq. (7) reduces to

$$\Lambda(\mathbf{k}) = \xi \Omega \frac{1}{k_B T} \alpha \tan\theta V_0^{-2/3} \left[\frac{1}{3} J \left(\frac{V_{\text{cr}}}{V_0} \right)^{1/3} + \lambda_{\text{elast}}(\mathbf{k}) \right], \quad (8)$$

where the elastic contribution to the amplification rate $\lambda_{\text{elast}}(\mathbf{k})$ is given by

$$\lambda_{\text{elast}}(\mathbf{k}) = -\frac{1}{6} \rho_0^3 \sum_b \exp(-i\mathbf{k} \cdot \mathbf{R}_{ab}) \frac{\partial^2}{\partial V_a \partial V_b} \times \left[\sum_c \sum_{d \neq c} \frac{V_c V_d}{R_{cd}^3} F\left(\frac{\rho_c}{R_{cd}}, \frac{\rho_d}{R_{cd}}\right) \right]. \quad (9)$$

F equals unity. However, it increases rapidly, if islands tend to touch ($\eta_1 + \eta_2 \rightarrow 1$).

When the system is subject to annealing, islands exchange material via the adatom sea. If the evolution kinetics of the island system is limited by the attachment or detachment of adatoms to the island perimeter, island evolution is governed by the difference in chemical potentials between any given island (μ_a) and the adatom sea ($\bar{\mu}$) [17],

$$\frac{dV_a}{dt} = \frac{\xi V_a^{1/3}}{k_B T} [\bar{\mu} - \mu_a]. \quad (5)$$

Here, ξ is a kinetic coefficient, and the chemical potential of the a th island is defined as

$$\mu_a = \Omega \frac{\partial E_{\text{total}}}{\partial V_a}, \quad (6)$$

where Ω is the atomic volume. The chemical potential of the adatom sea $\bar{\mu}$ is determined by mass conservation, $\sum_a dV_a/dt = 0$.

To elucidate the role of short-range elastic interactions on the stability of islands, we carry out a linear stability analysis of Eq. (5). Consider an array of cones placed at the sites of an ideal 2D hexagonal lattice, the volumes of the islands being slightly perturbed around the average volume such that $V_a = V_0 + \delta V_a$. Assuming $\delta V_a = \text{const} \times \exp(i\mathbf{k} \cdot \mathbf{R}_a)$, we substitute it into (5), evaluate the chemical potential via Eqs. (1), (3), and (6), linearize the equation, and seek the temporal evolution in the form $\delta V_a(t) = \text{const} \times \exp(i\mathbf{k} \cdot \mathbf{R}_a) \exp(\Lambda t)$. This yields the expression for the amplification rate Λ ,

Results for $\lambda_{\text{elast}}(\mathbf{k})$ are shown in Fig. 1. It follows from Figs. 1(c) and 1(d) that the most unstable modes are fluctuations at the K point of the first Brillouin zone (BZ). Figure 1(e) displays island volume fluctuations in this mode revealing that the array of islands tends to ripen into a less dense hexagonal array with the shaded islands growing and the open circles shrinking. Figure 1(f) shows the amplification rate λ_{elast} at the K point of the BZ as a function of the surface coverage q . The maximum coverage $q_{\text{max}} = \pi/(2\sqrt{3}) \approx 0.9068$ refers to a case where every island touches its nearest neighbors. It follows from Fig. 1(f) that, in a narrow interval of the coverage q , namely $0.8845 \leq q \leq 0.9068$, the elastic contribution to λ_{elast} is negative, i.e., the elastic interaction between islands stabilizes the array of cones against ripening.

The stabilizing contribution of the elastic interaction competes with the destabilizing contribution of the surface energy given by the first term in Eq. (8). Figure 2 contains the phase diagram in variables

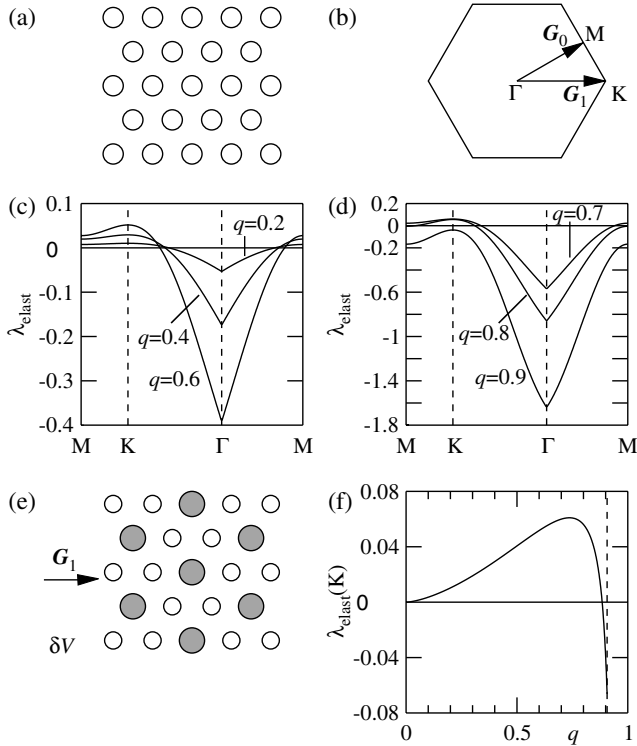


FIG. 1. Effect of elastic interaction on the stability of an array of cones. (a) Plan view of the ideal hexagonal lattice of equal-volume cones. (b) The first Brillouin zone (BZ) of the reciprocal lattice. (c), (d) The contribution of the elastic interaction to the amplification rate of fluctuations of island volumes $\lambda_{\text{elast}}(\mathbf{k})$ for different surface coverage q . Negative values of λ_{elast} correspond to stable modes, and positive values refer to instability. (e) Fluctuations of island volumes in the most unstable mode at the K point of the BZ. Open and shaded circles represent shrinking and growing islands, respectively. (f) The amplification rate $\lambda_{\text{elast}}(\mathbf{k})$ at the K point of the BZ as a function of coverage q .

$\rho_0/\rho_{\text{cr}} = (V_0/V_{\text{cr}})^{1/3}$ and coverage q , showing parameter regions corresponding to unstable and metastable arrays of cones.

It should be noted that the elastic interaction between islands becomes stabilizing if islands are very close and nearly touch each other. Two neighboring cones touch each other at a single point, whereas two pyramid-shaped islands touch each other along a line. Thus, one may expect that an array of pyramids will be metastable over a considerably wider parameter region.

To numerically verify and further investigate the stability regime, we have performed ripening simulations based on Eq. (5). In these simulations, strained island arrays are constructed with $\rho_0/\rho_{\text{cr}} \approx 53$, which from Fig. 2 gives a critical coverage of $q \approx 88.8\%$ above which the array is metastable. Consider an array of cones positioned on the sites of a hexagonal lattice with the island radii randomly perturbed about their average value. For a coverage of 89.3%, which is above the critical coverage for stability, the island radii converge to a common value,

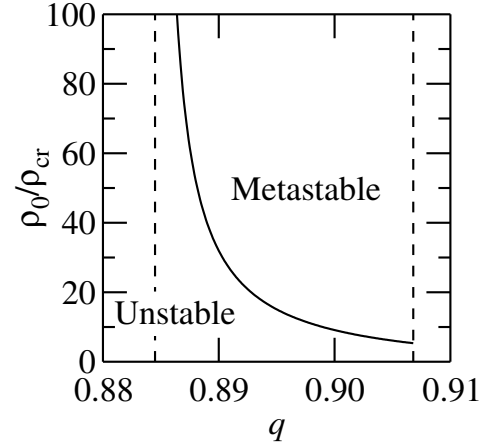


FIG. 2. Phase diagram for a hexagonal array of cones as a function of surface coverage q and basal radius ρ_0/ρ_{cr} .

confirming that near-field elastic interactions stabilize the array against small fluctuations in volume [Fig. 3(a)]. Removing the strain [Fig. 3(b)] results in coalescence [18]. This is included by assuming that, when two islands of volume V_a and V_b come into contact through their growth, they are replaced spontaneously by a single island of volume $V_a + V_b$ positioned at the center of mass of the two previous islands. Multiple coalescence events

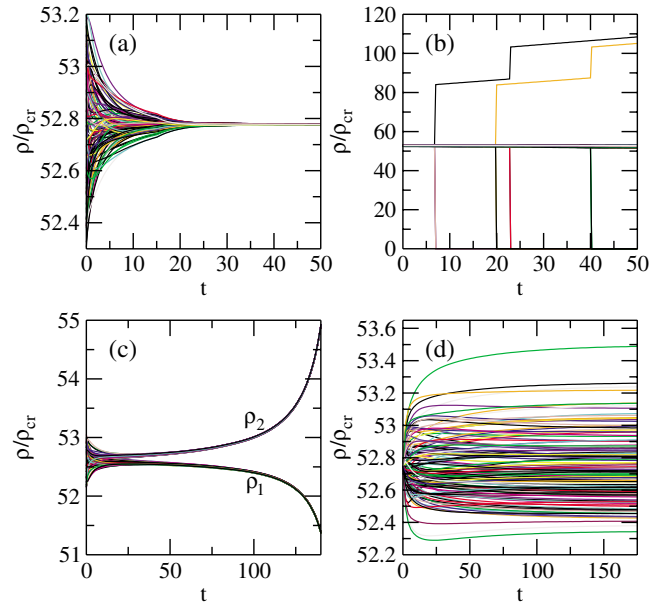


FIG. 3 (color). Time evolution of island radii for a hexagonal array with (a) perturbed radii, strain included; (b) perturbed radii, no strain; (c) perturbed radii, strain included; (d) perturbed positions, strain included. Evolutions in (a) and (d) correspond to metastable configurations (see text). Discontinuous jumps in radii in (b) correspond to coalescence events and indicate instability. Radii in the strained cases are measured in units of the critical radius for nucleation ρ_{cr} . Radii in the unstrained case are measured in the same units for comparison. Time is in scaled units.

are modeled likewise. Coalescence events manifest themselves as discontinuous jumps in island radii in Fig. 3(b).

In Fig. 3(c), we consider the time evolution of a hexagonal array for a coverage of 88.5%, which is just below the critical coverage required for metastability. The randomly perturbed radii split into two diverging bands, labeled ρ_1 and ρ_2 , demonstrating the instability of the array to small perturbations in radii at this coverage. The physical significance of the two bands can be directly associated with the most unstable mode represented in Fig. 1(e). In this ordered superlattice structure, island radii belonging to the high band (ρ_2) are surrounded by nearest neighbors corresponding to the low band (ρ_1).

Finally, we comment on the stability of the array with respect to island positions. Consider an array of equal volume islands placed in perturbed positions around the sites of a hexagonal lattice. In Fig. 3(d), we consider the time evolution of island radii for an array with a coverage of 89.2%. Initially, the radii diverge from the common starting value before reaching a metastable configuration in which individual islands have the same chemical potential. Therefore, metastability also exists with respect to perturbed island positions as well as volumes.

It is known that elastic interactions also play an essential role in the evolution of particle morphology and interparticle spatial correlations during Ostwald ripening in bulk coherent solids. This nonclassical ripening behavior can include particle shape transitions, spontaneous splitting, and alignment [19]. Precipitates can form structural arrangements which are metastable or even completely stable against coarsening [20]. The stability of these structures is highly sensitive to the details of the interaction including elastic anisotropy and the difference in elastic moduli between the particles and matrix. A general tendency for the enhancement of stability against ripening is observed in less symmetric geometries which is also very likely to manifest itself in the case of surface arrays of strained islands.

Our model of interacting strained conical islands reproduces the important properties of faceted islands associated with a nonzero contact angle with the wetting layer, including the strain and stress singularity at the base perimeter. We emphasize that the analysis neglects the possibility of island shape changes induced by interdot diffusional or elastic interactions. If these effects occur, they will modify the region of stability.

In summary, we have shown that short-range elastic interactions between coherently strained conical islands can stabilize dense arrays against ripening, leading to a finite region of metastability. Although it seems unlikely that such dense regimes can be realized experimentally, the formal existence of a metastable regime is of important conceptual significance in the fields of cluster stability and coarsening dynamics. Furthermore, the ap-

plication of this approach to other, less symmetric, island geometries is likely to enhance the metastability region and open up new possibilities to experimentally obtain uniformly sized quantum dot arrays.

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- [1] M. Zinke-Allmang, *Thin Solid Films* **346**, 1 (1999).
- [2] C. Teichert, *Phys. Rep.* **365**, 335 (2002).
- [3] D. Bimberg, M. Grundmann, and N. N. Ledentsov, *Quantum Dot Heterostructures* (Wiley, Chichester, 1998).
- [4] V. A. Shchukin and D. Bimberg, *Rev. Mod. Phys.* **71**, 1125 (1999).
- [5] D. E. Jesson, in *Properties of Silicon Germanium and SiGe:Carbon*, edited by E. Kasper and K. Lyutovich, EMIS Data reviews Series, No. 24 (INSPEC, London, 2000), Chap. 1.1, p. 3.
- [6] M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, *Surf. Sci. Rep.* **16**, 377 (1992).
- [7] G. R. Carlow, R. J. Barel, and M. Zinke-Allmang, *Phys. Rev. B* **56**, 12519 (1997).
- [8] I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961).
- [9] B. K. Chakraverty, *J. Phys. Chem. Solids* **28**, 2401 (1967).
- [10] V. A. Shchukin, N. N. Ledentsov, P. S. Kop'ev, and D. Bimberg, *Phys. Rev. Lett.* **75**, 2968 (1995).
- [11] I. Daruka and A.-L. Barabási, *Phys. Rev. Lett.* **79**, 3708 (1997).
- [12] G. Medeiros-Ribeiro, A. M. Bratkovski, T. I. Kamins, D. A. A. Ohlberg, and R. S. Williams, *Science* **279**, 353 (1998).
- [13] J. Tersoff and R. M. Tromp, *Phys. Rev. Lett.* **70**, 2782 (1993).
- [14] J. Tersoff and F. K. LeGoues, *Phys. Rev. Lett.* **72**, 3570 (1994).
- [15] J. A. Floro, M. B. Sinclair, E. Chason, L. B. Freund, R. D. Twisten, R. Q. Hwang, and G. A. Lucadamo, *Phys. Rev. Lett.* **84**, 701 (2000).
- [16] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1970).
- [17] F. M. Ross, J. Tersoff, and R. M. Tromp, *Phys. Rev. Lett.* **80**, 984 (1998).
- [18] D. Beysens, C. M. Knobler, and H. Schaffar, *Phys. Rev. B* **41**, 9814 (1990).
- [19] P. W. Voorhees, *Annu. Rev. Mater. Sci.* **22**, 197 (1992).
- [20] A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).