Spontaneous Ordering of Arrays of Coherent Strained Islands

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The energetics of an array of *three-dimensional* coherent strained islands on a lattice-mismatched substrate is studied. The contribution of the edges of islands to the elastic relaxation energy *always has a minimum* as a function of the size of an island L, and the total energy $E(L)$ *may have a minimum* at an optimum size $L_{\rm opt}$. Among different arrays of islands on the (001) surface of a cubic crystal, the total energy is minimum for the 2D *periodic square lattice* with primitive lattice vectors along "soft" directions [100] and [010]. This is a *stable* array of islands which do not undergo ripening.

Spontaneous formation of ordered nanostructures on crystal surfaces is at present a subject of active experimental and theoretical research. One mechanism of formation is periodic faceting [1–3] observed on various vicinal, low-index, and high-index surfaces [4]. The theory of Ref. [3] shows that a periodically corrugated surface corresponds to the minimum of the free energy $E = E_{\rm facets} + E_{\rm edges} + \Delta E_{\rm el}$, where $E_{\rm facets}$ is the free energy of facets, $E_{\rm edges}$ is the short-range energy of edges, and $\Delta E_{\rm el}$ is the elastic relaxation energy, caused by the discontinuity of the intrinsic surface stress tensor τ_{ij} at crystal edges.

Another class of self-assembled nanostructures is associated with periodically ordered structures of surface domains, e.g., with ordered arrays of monolayer-height islands in heterophase systems [5]. The theory of Refs. [6,7] shows that a 1D periodic domain structure corresponds to the minimum of the free energy $E = E_{\rm bound} + \Delta E_{\rm el}$, where $E_{\rm bound}$ is the energy of domain boundaries and $\Delta E_{\rm el}$ is the elastic relaxation energy. The energetics of a dilute array of strained islands was studied in Ref. [8] for the case where islands have a planar top surface, and the height of islands is *kinetically limited* to a value considerably smaller than the lateral size. In Ref. [9], a relation was established between the size of a single surface domain (for low domain concentration) and the minimum separation between them at intermediate concentration.

On the other hand, the crystal growth on a lattice-mismatched substrate often proceeds via formation of *essentially three-dimensional islands* [10–14] on the bare substrate surface for Volmer-Weber (VW) growth or on the wetted surface for coherent Stranski-Krastanow (SK) growth. Formation of *three-dimensional* islands leads in SK growth mode to a reduction of the strain energy and to an increase of the surface energy as compared to the planar case [15,16]. The former is proportional to the volume of the island, and the latter is proportional to the surface area of the island. If the size of a three-dimensional island exceeds a critical size, further growth of the island becomes energetically favorable. It is generally assumed that, if the material supply is interrupted, the further growth of large

islands occurs at the expense of the evaporation of smaller islands, islands are thus undergoing ripening.

Surprisingly, experiments show in most cases rather narrow size distribution of the islands [12–14], which does not follow from the SK growth mode itself. Besides that, the authors of Ref. [14] have reported that coherent islands of InAs form, under certain conditions, a quasiperiodic square lattice on the GaAs(001) surface. The periodicity and the island size do not change with time.

Experimental results of Ref. [14] indicate the existence of a new class of self-assembled nanostructures, namely, ordered arrays of coherent strained *three-dimensional islands*. Here we study the energetics of an array of such islands under the constraint of the fixed amount of the deposited material Q assembled in all islands, where Q is defined in numbers of monolayers. We treat both the substrate and the deposited material as *elastically anisotropic cubic media* with equal elastic moduli λ_{ijlm}, and the lattice mismatch between the two materials being equal to $\epsilon_0 = \Delta a/a$, where a is the lattice spacing.

The energy of a uniformly strained film of thickness (Qa) on a (001) substrate is given by $E_{\rm el}^{(0)} = \lambda \epsilon_0^2 A(Qa)$, where the elastic modulus λ equals $(c_{11} + 2c_{12})(c_{11} - c_{12})c_{11}^{-1}$, c_{11} and c_{12} are elastic moduli in the Voigt notation, and A is the surface area. The change of the energy of the heterophase system due to the formation of a single island is

$$\Delta \widetilde{E}_{\rm isl} = \Delta \widetilde{E}_{\rm facets} + \widetilde{E}_{\rm edges} + \Delta \widetilde{E}_{\rm el}. \qquad (1)$$

Here $\Delta \widetilde{E}_{\rm facets} = \int [\gamma(\hat{\bf m})(\hat{\bf m} \cdot \hat{\bf n})^{-1} - \gamma(\hat{\bf n})] dA$, where $\gamma(\hat{\bf m})$ is the surface energy of the tilted facet with the orientation $\hat{\bf m}$, and $\hat{\bf n} = (0, 0, 1)$ is the normal to the flat surface. We assume for simplicity that the quantity $\gamma(\hat{\bf m})(\hat{\bf m} \cdot \hat{\bf n})^{-1}$ has, besides the *cusped* absolute minimum for the (001) surface, also *cusped local minima* for four equivalent facets, $(k0l)$, $(0kl)$, $(\bar{k}0l)$, and $(0\bar{k}l)$. Then, under a range of conditions, the minimum of $\Delta \widetilde{E}_{\rm isl}$ will correspond to an island bound by $(k0l)$, $(0kl)$, $(\bar{k}0l)$, and $(0\bar{k}l)$ facets, e.g., to a pyramid or to a prism as shown in the inset of Fig. 1.
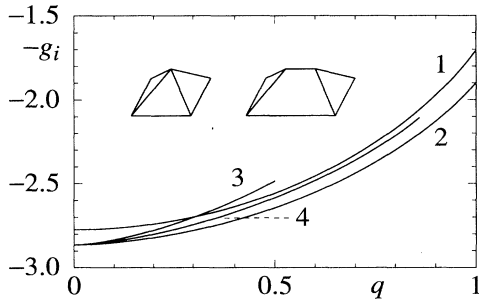

FIG. 1. The energy per unit area $\Delta E_{\mathrm{el}}^{(1)} + E_{\mathrm{inter}} = (Qa)\tilde{\lambda}\epsilon_0^2\varphi_0 \times [-g_i(q)]$ for different arrays of coherent strained islands versus the fraction q of the surface covered by islands. (1) 1D array of elongated prisms; (2) 2D square lattice of pyramids with primitive lattice vectors $(1,0,0)$ and $(0,1,0)$. (3) 2D "checkerboard" square lattice of pyramids with primitive lattice vectors $(1,-1,0)$ and $(1,1,0)$. (4) 2D hexagonal lattice of pyramids with primitive lattice vectors $(-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0)$ and $(1,0,0)$. Curves 3 and 4 terminate at maximum possible coverages for given arrays. The inset shows schematic shapes of islands.

The second term in Eq. (1), $\tilde{E}_{\mathrm{edges}}$, is the short-range energy of edges. The third term, $\Delta\tilde{E}_{\mathrm{el}}$, is the change of the strain energy due to elastic relaxation, termed below "the elastic relaxation energy." For lattice-mismatched systems with edges, there are two sources of the strain field, namely, the lattice mismatch ϵ_0 and the discontinuity of the intrinsic surface stress tensor τ_{ij} at the edges. Therefore $\Delta\tilde{E}_{\mathrm{el}}$ is a quadratic function of ϵ_0 and τ. The dependence of $\Delta\tilde{E}_{\mathrm{el}}$ on the size of an island L is determined by the scaling properties of the equilibrium equations of elasticity theory [17],

$$\Delta\tilde{E}_{\mathrm{el}} = - f_1(\varphi_0)\lambda\epsilon_0^2 L^3 - f_2(\varphi_0)\epsilon_0\tau L^2$$
$$- f_3(\varphi_0)\frac{\tau^2}{\lambda} L \ln\left(\frac{L}{2\pi a}\right), \qquad (2)$$

where the coefficients $f_1, f_2, f_3, \ldots$, depend only on the

tilt angle of facets φ, and $\varphi_0 = \tan^{-1}(k/l)$. The first term in Eq. (2) is the contribution of the lattice mismatch to the elastic relaxation energy $\Delta\tilde{E}_{\mathrm{el}}^{(1)}$. Detailed analysis of Ref. [17] shows that the term $-f_2(\varphi_0)\tau\epsilon_0 L^2$ is

$$-f_2(\varphi_0)\tau\epsilon_0 L^2 = - \int u_i^{(1)}(\mathbf{r}) \frac{\partial}{\partial r_j} \tau_{ij}(\mathbf{r})\, dA - \tau_{ij}^{(\mathrm{facets})}$$
$$\times \delta_{ij}\epsilon_0 \sec\varphi_0 L^2 + \tau_{ij}^{(\mathrm{flat})}\delta_{ij}\epsilon_0 L^2, \qquad (3)$$

where $u_i^{(1)}(\mathbf{r})$ is the contribution of the lattice mismatch to the elastic displacement field. The first term in Eq. (3) is the interaction term of two strain fields, due to the lattice mismatch on the one hand and to the surface stress discontinuity on the other hand. The second term in Eq. (3) is the renormalization of the surface energy of island facets due to the change of the lattice parameter on the facets, and the third term is the similar renormalization term for the flat surface. All three terms of Eq. (3) are proportional to L^2. It will be shown below that the quantity $-f_2(\varphi_0)\tau\epsilon_0 L^2$ is very important for the possibility of ordering of three-dimensional islands, because it can reduce significantly the surface energy of island facets. The term $-f_2(\varphi_0)\tau\epsilon_0 L^2$ will be called, for convenience, the mismatch-induced renormalization of the surface energy of island facets.

The third term in Eq. (2) is the contribution of the edges to the elastic relaxation energy $\Delta\tilde{E}_{\mathrm{el}}^{(2)}$. We consider islands of size larger than the critical one, the first term in Eq. (2) being the dominant contribution to $\Delta\tilde{E}_{\mathrm{el}}$. For such islands, the square-based pyramid is energetically more favorable than the elongated prism, i.e., the "quantum dot" is more favorable than the "quantum wire," because it provides larger elastic relaxation [18].

For a *dilute* system of islands, the elastic interaction between islands via the strained substrate may be neglected. Then, substituting $\Delta\tilde{E}_{\mathrm{el}}$ from Eq. (2) into Eq. (1), summing contributions of identical pyramid-shaped islands, one gets the energy of the dilute system of islands *per unit surface area* as follows:

$$E_{\mathrm{dilute}}(L) = (Qa)(6\cot\varphi_0)\left[- f_1(\varphi_0)\lambda\epsilon_0^2 + \frac{\gamma(\varphi_0)\sec\varphi_0 - \gamma(0) - f_2(\varphi_0)\tau\epsilon_0}{L} + \frac{\eta f_4(\varphi_0)}{L^2} - \frac{\tau^2 f_3(\varphi_0)}{\lambda L^2} \ln\left(\frac{L}{2\pi a}\right)\right].$$
$$(4)$$

Here the first term is the contribution of the lattice mismatch to the elastic relaxation energy $\Delta E_{\mathrm{el}}^{(1)}$. The second term is the renormalized surface energy of the island. The third term is the short-range energy of island edges, η being the characteristic energy per unit length of the edge. The last term, which is the contribution of the edges to the elastic relaxation energy, $\Delta E_{\mathrm{el}}^{(2)} \sim -L^{-2}\ln L$, always has a minimum as a function of L.

For a *dense* system of islands, elastic interaction between islands via the strained substrate becomes essential. The system of interacting islands is then a system of stress

domains where the minimum of the strain energy corresponds to a *periodic domain structure* [6,7,9,19,20]. In the approximation of small tilt angle of facets φ_0, the sum of the energy per unit surface area $\Delta E_{\mathrm{el}}^{(1)}$ for isolated islands and of the interaction energy per unit surface area E_{inter} is $\Delta\tilde{E}_{\mathrm{el}}^{(1)} + E_{\mathrm{inter}} = (Qa)\tilde{\lambda}\epsilon_0^2\varphi_0 \times [-g_i(q)]$. Here $\tilde{\lambda} = (c_{11} + 2c_{12})^2 (c_{11} - c_{12})^3 c_{11}^{-3}(c_{11} + c_{12})^{-1}$, q is the fraction of the surface covered by islands, and the functions $-g_i(q)$ for different arrays of islands are displayed in Fig. 1.

Among different 2D arrays of pyramid-shaped islands on the (001) surface of an elastically anisotropic cubic medium, the minimum energy corresponds to a 2D square lattice of islands with primitive lattice vectors along the "soft" directions [100] and [010]. There exist two factors that favor the square lattice. First is the cubic anisotropy of elastic moduli of the medium, and second is the square shape of the base of a single island.

The approximation of small tilt angles used in deriving $\Delta E_{\mathrm{el}}^{(1)} + E_{\mathrm{inter}}$ in Fig. 1 gives significant elastic relaxation energy already for small φ_0, in agreement with Ref. [16]. For large values of φ_0, this approximation overestimates the elastic relaxation energy (it yields -64% of the strain energy of a flat film for $\varphi_0 = 45°$). Calculations by the finite element method for $\varphi_0 = 45°$ show basically similar results to those of Fig. 1 [18]. First, the elastic relaxation energy is more efficient for pyramids, where it equals -60% of the strain energy of a flat film, than for elongated prisms, where it is -45%. Second, the cubic anisotropy of elastic moduli also favors in this case a 2D *square* lattice of islands with primitive lattice vectors along the "soft" directions [100] and [010].

The main part of the interaction energy is the energy of dipole-dipole elastic repulsion between islands, $E_{\mathrm{inter}} = (Qa)6\cot\varphi_0 f_5(\varphi_0)\lambda\epsilon_0^2 q^{3/2}$. Thus the curve $-g_2(q)$ in Fig. 1 in the region $0 \le q \le 0.5$ can be approximated by $-g_2(q) = -2.87 + 0.61q^{3/2}$ with the accuracy 0.01. To express q in terms of Q and L, we equate the volume of the pyramid and the volume of the initially uniform film per unit period $D \times D$ of the square lattice, $(1/6)L^3\tan\varphi_0 = D^2(Qa)$. Hence, $q \equiv L^2/D^2 = 6Qa \times \cot\varphi_0/L$. Now, adding $E_{\mathrm{inter}} \sim q^{3/2} \sim L^{-3/2}$ to the energy of Eq. (4), we get the energy of the array of interacting islands. To consider in detail L-dependent terms in the energy per unit area $E(L) = E_{\mathrm{dilute}}(L) + E_{\mathrm{inter}}(L)$, we introduce the characteristic length

$$L_0 = 2\pi a \times \exp\left[\frac{f_4(\varphi_0)\eta\lambda}{f_3(\varphi_0)\tau^2} + \frac{1}{2}\right], \qquad (5)$$

and the characteristic energy per unit area, $E_0 = (Qa)3\cot\varphi_0 f_3(\varphi_0)\tau^2\lambda^{-1}L_0^{-2}$. Then the sum of all L-dependent terms in $E(L)$ may be written as a function of the dimensionless length L/L_0,

$$E(L) = E_0\left[-2\left(\frac{L_0}{L}\right)^2\ln\left(\frac{e^{1/2}L}{L_0}\right)\right.$$
$$\left. + \frac{4\beta}{e^{3/4}}\left(\frac{L_0}{L}\right)^{3/2} + \frac{2\alpha}{e^{1/2}}\left(\frac{L_0}{L}\right)\right]. \quad (6)$$

This function is governed by two control parameters,

$$\alpha = [\gamma(\varphi_0)\sec\varphi_0 - \gamma(0) - f_2(\varphi_0)\tau\epsilon_0] \times \frac{e^{1/2}\lambda L_0}{f_3(\varphi)\tau^2}, \qquad (7a)$$

$$\beta = (Qa)^{3/2} \times \frac{e^{3/4}f_5(\varphi_0)(6\cot\varphi_0)^{3/2}(\lambda\epsilon_0)^2 L_0^{1/2}}{2f_3(\varphi_0)\tau^2}. \qquad (7b)$$

Here α is the ratio of the renormalized surface energy and of the contribution of edges to the elastic relaxation energy $|\Delta E_{\mathrm{el}}^{(2)}|$. As noted above, $\gamma(\varphi_0)\sec\varphi_0 - \gamma(0) > 0$. However, due to mismatch-induced renormalization of the surface energy of island facets, $-f_2(\varphi_0)\tau\epsilon_0$, the parameter α can be *of either sign*. The parameter β is the ratio $E_{\mathrm{inter}}/|\Delta E_{\mathrm{el}}^{(2)}|$; it increases with the amount of the deposited material as $Q^{3/2}$.

Searching the minima of the energy $E(L)$ from Eq. (6) for different α and β, we obtain the phase diagram of Fig. 2. For the region 1 of the phase diagram, there exists an optimum size of islands L_{opt}, corresponding to the absolute minimum of the energy, $\min E(L) \equiv E(L_{\mathrm{opt}}) < 0$. On the other hand, the ripening of islands would correspond to $L \to \infty$ where the energy $E(L) \to 0$. It means that the 2D periodic square lattice of islands of the optimum size L_{opt} is a *stable array*, and *islands do not undergo ripening*. For region 2 of the phase diagram, there exists only a local minimum of the energy, corresponding to a metastable array where $E(L') > 0$. For region 3, the local minimum in the energy $E(L)$ disappears. In both regions 2 and 3, there exists the thermodynamic tendency to ripening. If the system initially corresponds to the region 1, and the amount of the deposited material Q increases, then the point in the phase diagram moves to regions 2 and 3, and islands undergo ripening.

If $\alpha \le 0$, there exists an absolute minimum of the energy $E(L)$ for an arbitrary value of β, and $\min E \equiv E(L_{\mathrm{opt}}) < 0$. Besides the absolute minimum of $E(L)$, there may also exist a local minimum at $L = L'$, the energy of a corresponding metastable state $E(L') < 0$ in region 4; $E(L') > 0$ in region 5; and no metastable state exists in region 6.

To estimate characteristic values of α and β, we substitute $\tau \approx 100$ meV/Å^2, $\lambda \approx 500$ meV/Å^3, $L_0 \approx 100$ Å, and $a = 2.8$ Å in Eq. (7b). This gives $\beta \approx 1$ for $|\epsilon_0| \approx 1\%$ and $Q = 0.5$ monolayers. Therefore, if $\alpha > 0$, the array of islands may correspond to region 1 of the phase
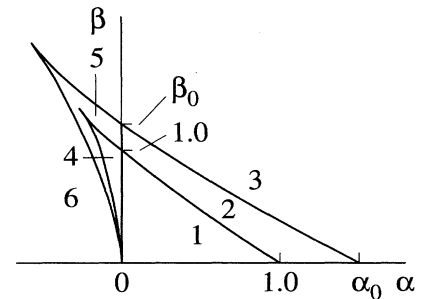

FIG. 2. Schematic phase diagram of the stability of square lattice of coherent strained islands in the plane of control parameters $\alpha - \beta$. Here α and β are defined in Eqs. (7a) and (7b). In regions 1, 4, 5, and 6, there exist stable arrays of islands that do not undergo ripening. In regions 2 and 3, all arrays of islands undergo ripening. $\alpha_0 = 2e^{-1/2} \approx 1.213$; $\beta_0 = (4/3)e^{-1/4} \approx 1.038$.

diagram only for low coverage Q. On the other hand, the typical difference in the surface energy between facets of different orientation is of the order of $\approx 5-10$ meV/Å^2 [21]. It follows then from Eq. (7a) that the parameter α for a strongly mismatched system may become negative due to mismatch-induced renormalization of the surface energy of island facets. If $\alpha < 0$, then the increase of $|\epsilon_0|$, e.g., by the increase of x for the heterophase system $In_xGa_{1-x}As/GaAs(001)$, results in the decrease of L_{opt}. This agrees with the experimental data of Ref. [14].

Comparing our theory with experimental data on the InAs/GaAs(001) system of Ref. [14], we outline that the molecular beam epitaxy (MBE) growth of 4 monolayers of InAs for $T = 480\,°C$ and As pressure $(1.5-3) \times 10^{-6}$ torr results in an array of 140 Å pyramid-shaped quantum dots arranged in a 2D square lattice with principal axes along the [100] and [010] directions. This array is stable and does not undergo ripening upon growth interruption.

Significant changes of MBE growth conditions ($T = 480\,°C$ and $P_{As} = 10^{-5}$ torr) lead to a ripening regime, which results in formation of large macroscopic islands. This indicates that kinetics is sufficient to drive the system to a state with lower energy, i.e., to a stable array for the ordering regime or to macroscopic clusters for the ripening regime. The shift from the ordering regime to the ripening regime may be caused by the As pressure-induced change of the surface reconstruction [22].

We emphasize that our conclusions do not depend on approximations made while deriving Eq. (4). For more detailed treatment, first, the above omitted entropy term in the free energy will lead to a finite concentration of the residual gas of adatoms on the surface and to a reduction of the total amount of material assembled in islands. Second, if the surface energy $\gamma(\hat{m})$ does not have cusped local minima, then the tilt angle of facets φ will vary with the size of the island. Neither of these effects prevents the possibility of formation of periodic arrays of coherent strained islands that do not undergo ripening upon growth interruption.

To conclude, we have shown that coherent strained *essentially three-dimensional* islands on a lattice-mismatched substrate form, under certain conditions, *stable* periodic arrays of equal-sized islands. For islands on the (001) surface of a cubic crystal, the arrangement in the 2D periodic square lattice with primitive lattice vectors oriented along the lowest-stiffness directions [100] and [010] is energetically preferred.

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