Structural Transition in Large-Lattice-Mismatch Heteroepitaxy

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The mechanisms of island nucleation, growth, and dislocation formation in large lattice-mismatch heteroepitaxy are analyzed theoretically. It is shown that 2D platelets tend to transform to 3D islands as they exceed a certain critical size. During island growth, the increase of the strain concentration at the island edge makes it increasingly difficult for adatoms to reach the island, which leads to the formation of homogeneously sized islands. The high strain concentration at the island edge is eventually relieved by growing-in of misfit dislocations. [S0031-9007(96)01513-X]

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The structural evolution of a thin film grown on a substrate with a lattice mismatch is a problem of considerable practical and theoretical interest. It has been demonstrated experimentally that in large lattice-mismatch ($>\sim 2\%$) semiconductor systems (e.g., Ge/Si [1–3], InGaAs/GaAs [4,5], and InGaAs/GaAs [6]) the epitaxial growth normally proceeds via the Stranski-Krastanow mode: A few monolayers (MLs) thick coherent wetting layer first grows on the substrate. Coherent (dislocation-free) islands then nucleate on top of the wetting layer. After these islands grow over a certain critical size, misfit dislocations form at the island edges to relieve the misfit strain. It is observed that the sizes of coherent islands are usually very uniform (with a deviation of $\sim 10\%$); such self-organized islands have been used as quantum dots [5]. These interesting phenomena have, in turn, sparked a significant amount of theoretical work.

At the initial stage of Stranski-Krastanow epitaxy, the sum of surface and interfacial energy is first reduced by the growth of a wetting layer up to a few MLs thick on the substrate surface. However, strain energy is built into the epilayer in order to fit its lattice with the lattice-mismatched substrate. This strain energy can be reduced during further growth by the formation of islands due to the possibility of atomic bonding distortion in an island (as illustrated in Fig. 1), but the surface energy is increased [7]. The change of the strain and surface energy has been calculated, which has shown that the decrease of strain energy can outweigh the increase of the surface energy when an island exceeds a critical size [8,9]. Therefore, it has been proposed that an island with a certain shape may nucleate by increasing its size [8]. It has also been proposed that a two-dimensional (2D) platelet can change its shape to form an island [10].

After an island is nucleated, thermodynamic calculations have shown that the system free energy decreases monotonically with increasing island size [8,9]. Without a free energy minimum at a certain island size, therefore, it is hard to explain why observed island sizes tend to be so uniform. It has been proposed that 2D platelets may have an energetic minimum at a certain size, which may lead to homogeneous size distribution of 2D platelets, leading to equal size islands assuming that the islands do not change their volume during nucleation [10]. However, the growth of 2D platelets is a kinetically controlled process; the size deviation for 2D platelets ($\sim 50\%$–100% [11]) is usually much larger than that for 3D islands ($\sim 10\%$).

When coherent islands grow over a certain critical size, misfit dislocations are observed to form at island edges where the highest strain exists [3,4,12]. Theoretical calculation has shown that the strain concentration at an island edge increases with island size; when it reaches a critical value, it will induce the formation of a dislocation [9].

We have studied experimentally the structural transition in large lattice-mismatch Ge/Si and InGaAs/GaAs systems [12,13]. In this Letter, theoretical models are proposed to understand: (i) the island nucleation process, (ii) the island growth process and the cause of the formation of uniformly sized islands, and (iii) dislocation formation mechanism in islands.

Figure 2(a) is an atomic force microscope (AFM) image of coherent Ge islands grown on a Si substrate by molecular beam epitaxy (MBE) at 500 °C. The islands were capped with Si at room temperature prior to removing the samples from the MBE chamber. A cross section transmission electron microscopy (TEM) image of a coherent Ge island is shown in Fig. 2(b). The experimental details have been reported elsewhere [13].

Within the framework of linear elastic theory, the stress in lattice-mismatched islands has been calculated analytically [8] and numerically [9,10]. (For a

FIG. 1. An atomic model illustrating, with exaggeration, the likely strain relaxation for atoms in an island (solid circles) bonding to substrate atoms (open circles) with a smaller lattice parameter.

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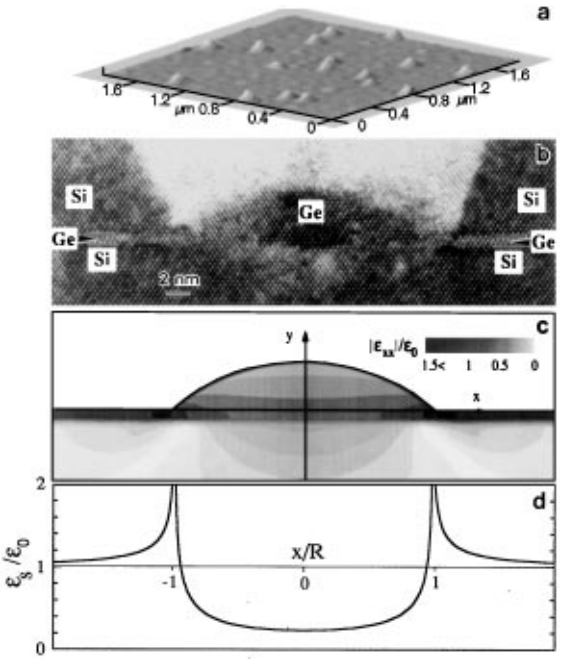

FIG. 2. (a) An AFM image of Ge islands grown on a Si substrate: (b) A cross-section TEM image showing a Ge island on a 6 MLs thick Ge wetting layer on a Si substrate: (c) The boundary of Ling's "mound" and a contour diagram showing the calculated strain ε_{xx} in the system: (d) The variation of surface strain ε_s along the system surface.

nanometer scale island, the stress calculated by continuum elastic theory should be considered as an estimation.) An analytic solution of the stress field in a 2D "mound" on a strained semi-infinite substrate is given by Ling [14]. The boundary of the "mound" is defined by $x = R\sinh(t)/[\cosh(t) + \cos(2\beta)]$, $y = R\sin(2\beta)/[\cosh(t) + \cos(2\beta)]$, with $-\infty \le t \le \infty$, where R is the island radius, β is defined in terms of the "mound" height h and radius R as $\tan(\beta) = h/R$. As shown in Fig. 2(c), it can be fitted well to the Ge island shown in Fig. 2(b) by allowing $\beta = 21°$. Therefore, the corresponding plane strain obtained from Ling's solution [14] can be treated as an approximation to the strain for a 3D island. A contour plot of the absolute value of the calculated strain ε_{xx} is also shown in Fig. 2(c), and the calculated surface tangential strain ε_s along the system surface is shown in Fig. 2(d). It can be seen that the strain ε_{xx} caused by lattice mismatch in the island is partially relaxed at the cost of inducing an extra strain in the substrate and increasing the strain in the wetting layer near the island edge.

The strain energy E_{strain} for islands with different boundaries defined by Ling can then be calculated by integrating the corresponding strain energy density over the whole system. The surface energy change E_{surface} for the system is approximately equal to $2\varepsilon_d h/h_0$, the sum of dangling bond energy, ε_d, at each atomic step, where h and h_0 are the heights of the island and a single step, respectively. As an example, the total energy change $E_t = E_{\text{strain}} + E_{\text{surface}}$ is calculated for Ge islands on a Si substrate, and E_t/E_0 is shown in Fig. 3 as a function of the angle β and N_i, the number of atoms in each x-y plane inside the islands, where E_0 is E_t under $\beta \to 0$, which is equal to the strain energy for a 2D platelet with an equal size N_i. The $\varepsilon_d = 0.8$ eV, shear moduli 7.90×10^{11} and 6.49×10^{11} dyn/cm^2 , Poisson's ratios 0.22 and 0.21, for Si and Ge, respectively [15], were used in the calculation. It can be seen from Fig. 3 that it is energetically unfavorable ($E_t > E_0$) for an island to form from a 2D platelet until its size is larger than a critical size N_c.

The N_c can also be derived analytically. It can be easily proved [9] that $E_t = E_{\text{strain}} + E_{\text{surface}} = \varepsilon_0^2 N_i f + N_i^{2/3} s$, where f and s are dimensionless quantities which depend only on the island shape and materials properties, but not on N_i or ε_0, the lattice mismatch. $\partial E_t/\partial\beta = \varepsilon_0^2 N_i \partial f/\partial\beta + N_i^{2/3}\partial s/\partial\beta$, where $\partial f/\partial\beta$ is negative but $\partial s/\partial\beta$ is positive. From $\partial E_t/\partial\beta = 0$, it can be obtained that

$$N_c = -\frac{1}{\varepsilon_0^6}\left(\frac{\partial f/\partial\beta}{\partial s/\partial\beta}\right)^3_{\beta=0}. \quad (1)$$

When a 2D platelet grows over the critical size N_c, $\partial E_t/\partial\beta < 0$, it becomes energetically unstable. During further deposition, the adatoms deposited on the wetting layer surface should tend to diffuse and hop to the top of the platelet, then a 3D island would be formed. *In situ* scanning tunneling microscopy has observed that the 3D islands are formed on the base of 2D platelets abruptly when they grow to a critical size [2].

The nucleated island density can be calculated as a function of deposition coverage θ. According to the scaling law [11], the density for the 2D (or multilayer) platelets with a size N $\rho(N,\theta) = (\theta/\overline{N}^2)\Phi(N/\overline{N})$, where $\Phi(N/\overline{N})$ is a scaling function which is independent with

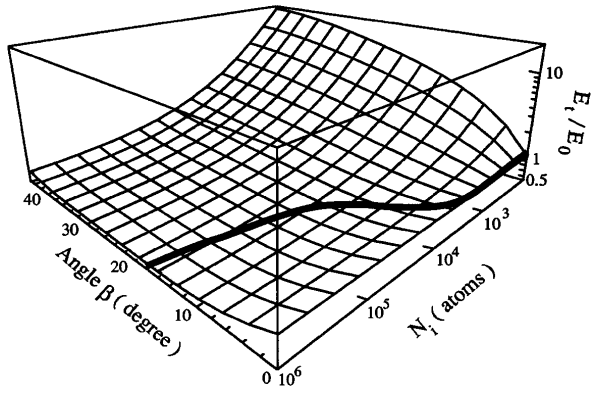

FIG. 3. The calculated E_t/E_0 for a Ge island on a Si substrate vs the island size N_i and the angle β. The trace of the minimum E_t/E_0 for islands with different sizes N_i is shown by the bold line.

$\overline{N}$. Then the 3D island density ρ_i at a coverage θ

$$\rho_i(\theta) = \int_{N_c}^{\infty} \rho(N,\theta)dN = \frac{\theta}{\overline{N}} \int_{N_c/\overline{N}}^{\infty} \Phi(u)du, \quad \text{with } u = \frac{N}{\overline{N}}. \qquad (2)$$

As an example, the density of InAs islands grown on a GaAs substrate is calculated as a function of coverage θ by assuming that $\Phi(u) = 1.1u\exp(-0.27u^{3.7})$, $\overline{N} \propto \theta$ [11], and $N_c = 5.1 \times 10^3$ atoms [as estimated from Eq. (1)]. The calculated $\rho_i(\theta)$ is shown in Fig. 4, and compared with the experimentally measured data [5]. $\overline{N}$ is taken to be equal to $4.6 \times 10^3\theta$ to fit the experimental data.

As $\overline{N}$ increases with θ to a value close to N_c, the density of the platelets with sizes larger than N_c, and therefore the density of islands increases dramatically vs θ (see Fig. 4). Since $N_c \propto 1/\varepsilon_0^6$ (see Eq. 1), the N_c at small lattice mismatches is much larger than that at large lattice mismatches. Therefore, at small lattice mismatch, platelets merge with each other to form a complete 2D epilayer before they can reach the critical size N_c, then the growth will proceed by the layer-by-layer mode. The island nucleation process could also be suppressed when the atomic surface diffusivity is reduced, e.g., by lowering growth temperature and/or using surfactant. The original kinetic surface morphology and local surface strain distribution may also have a profound influence on the island nucleation process [1,16].

Since $\partial E_t/\partial N_i = \varepsilon_0^2 f + \frac{2}{3}s/\sqrt[3]{N_i}$ decreases monotonically with N_i, during island growth it is energetically favorable for adatoms to attach to a larger island. *In situ* observation of the island growth process has shown that islands grow rapidly during the initial growth state; however, the growth rate slows down after the coherent islands reach certain sizes [3]. This experimental phenomenon cannot be explained by the thermodynamic model.

During island growth, the evolution of surface morphology is also influenced kinetically by the surface stress

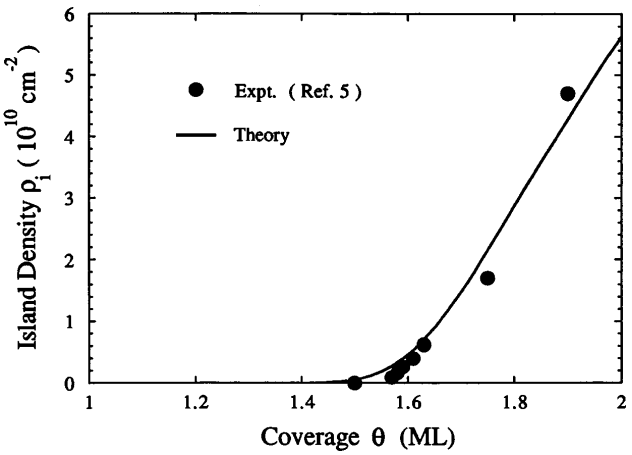

FIG. 4. Island density vs deposition coverage during the island nucleation stage.

since adatoms tend to diffuse on a surface away from sites with a higher strain to sites with a lower strain [7,16]. After an island forms, the strain relaxation in the island causes a strain concentration at the island edge [as shown in Fig. 2(d)], therefore, the adatoms deposited on the wetting layer surface will have to overcome an energy barrier $\Delta\mu_s$ before they can attach to the island. $\Delta\mu_s$ can be estimated quantitatively.

The island edge is geometrically similar to a notch. Based on the linear elastic solution for the strain field in a notch [17], the tangential strain ε_s on the wetting layer surface at a distance d from the island edge with $d \ll R$ has the form [9,17]

$$\varepsilon_s = B\varepsilon_0\left(\frac{R}{d}\right)^n, \qquad (3)$$

where n and B are constants determined only by the angle β. n varies from 0 to 0.46 as β changes from 0° to 45°. B is a preconstant, which can be determined by comparing Eq. (3) with Ling's solution [9,17]. The chemical potential for an atom on a strained surface can be written as [7] $\mu_s = \mu_0 + \frac{1}{2}\Omega c_s\varepsilon_s^2$, where μ_0 is the chemical potential on the surface with the same morphology but without strain, Ω is the volume of a lattice site, and c_s is the stiffness. By substituting Eq. (3) into the later equation, the energy barrier $\Delta\mu_s$, which is approximately equal to $\mu_s - \mu_0$ at an atomic distance a_0 from the island edge, can be derived as $\Delta\mu_s = C\varepsilon_0^2R^{2n}$, with $C = \Omega c_s B^2/2a_0^{2n}$. (Because of the large magnitude of the strains at the island edge, the calculated $\Delta\mu_s$ is only a first order approximation, but it should capture important qualitative physics.) Then the island growth rate takes the form

$$j \approx \pi R^2 F + \pi L^2 F \exp\left(-\frac{C\varepsilon_0^2R^{2n}}{kT}\right), \qquad (4)$$

where F is the deposition rate, T is the growth temperature, L is the free diffusion length for adatoms on the wetting layer surface. The first term on the right side of Eq. (4) is due to the accumulation of adatoms directly deposited onto the island surface; the second term is due to the accumulation of adatoms which are deposited on the wetting layer surface and then diffuse to the island. Adatoms deposited on the wetting layer surface within a distance L from the island edge could overcome the energy barrier $\Delta\mu_s$ to attach to the islands.

As an example, the growth rate dR/dt for a Ge island on a Ge wetting layer on a Si substrate is calculated based on Eq. (4) and shown in Fig. 5. $T = 500$ °C, $F = 0.3$ ML/s, $c_s = 12.61 \times 10^{11}$ dyn/cm^2 [15], and $L \approx 400$ Å (the experimentally measured average distance between the Ge islands) were used in the calculation. As shown in Fig. 3, the increase of angle β with respect to size N_i is dramatic during the nucleation process but becomes minor during growth (as observed experimentally [2,5]), therefore, as a approximation, it is assumed that during growth $\beta = 21°$, it can then be

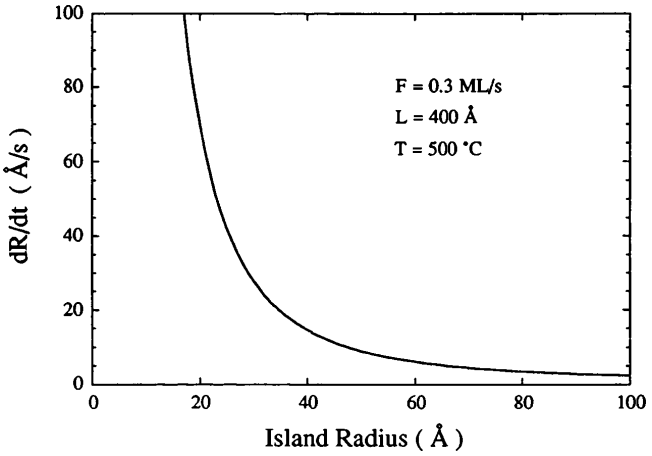

FIG. 5. Island growth rate vs island radius for a Ge island grown on a Si substrate.

derived that the corresponding $n \approx 0.19$ and $B \approx 1.03$. From Fig. 5, it can be seen that the island radius increases rapidly when the island size is small, which is mainly due to the accumulation of adatoms deposited on the wetting layer surface since $L \gg R$. However, each new adatom attached to the island tends to increase the strain concentration at the island edge, therefore, the energy barrier $\Delta\mu_s$ increases monotonically with increasing island radius R, which eventually slows down the island growth rate. The larger islands grow more slowly than the smaller islands, leading to the homogeneous distribution of island size, as is observed experimentally [2,3,5,6].

Since $\Delta\mu_s$ is proportional to ε_0^2, smaller coherent islands have been observed for larger lattice mismatch [1–6,12,13]. An increase of the growth temperature permits atoms to overcome the energy barrier $\Delta\mu_s$ more easily, therefore, the observed island size increases with increasing growth temperature [6].

When island sizes increase further, misfit dislocations are eventually formed at the island edges locally relieving the strain concentration. We have observed that the sessile Frank partial dislocations are usually at first formed at the edges of InGaAs islands on a GaAs substrate [12]. As shown in Eq. (3), the strain concentration at the island edge increases monotonically with island size; when it exceeds a critical value, the free energy for atoms to occupy the normal position A at the island edge may become higher than that for atoms to occupy a crystallographically "wrong" but less strained position B (see Fig. 1), then additional adatoms may tend to attach to position B thus nucleating a Frank partial dislocation [12]. It has been observed experimentally that the formation of the misfit dislocation, which relieves the strain concentration at the island edge, permits resumption of rapid growth until it reaches a second critical size [3]. A repeat of this process finally leads to the formation of large islands with a misfit dislocation network in the interface.

In summary, during initial epitaxial growth, the adatoms tend to attach to the edges of 2D atomic platelets to reduce dangling bond energy (or surface energy). When a platelet grows over a certain critical size, it becomes energetically favorable for adatoms to diffuse to the top of the platelet to form a 3D island to reduce the misfit strain energy. However, the strain relaxation in the island causes a strain concentration near the island edge, which then results in a kinetic barrier for adatoms to diffuse to the islands, therefore island growth rate is slowed down gradually as island size increases, leading to the formation of homogeneously sized islands. When islands grow further, the increasing strain concentration at the island edge eventually makes it energetically favorable for adatoms to attach to a crystallographically "wrong" position to nucleate a misfit dislocation.

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[1] Y. W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).
[2] B. Voigtlander and A. Zinner, Appl. Phys. Lett. **63**, 3055 (1993).
[3] F. K. LeGoues, M. C. Reuter, J. Tersoff, M. Hammar, and R. M. Tromp, Phys. Rev. Lett. **73**, 300 (1994).
[4] S. Guha, A. Madhukar, and K. C. Rajkumar, Appl. Phys. Lett. **57**, 2110 (1990).
[5] D. Leonard, K. Pond, and P. M. Petroff, Phys. Rev. B **50**, 11 687 (1994).
[6] M. Sopanen, H. Lipsanen, and J. Ahopelto, Appl. Phys. Lett. **67**, 3768 (1995).
[7] D. J. Srolovitz, Acta Metall. **37**, 621 (1989).
[8] J. Tersoff and F. K. LeGoues, Phys. Rev. Lett. **72**, 3570 (1994).
[9] L. B. Freund, H. T. Johnson, and R. V. Kukta, Mater. Res. Soc. Symp. Proc. (to be published).
[10] C. Priester and M. Lannoo, Phys. Rev. Lett. **75**, 93 (1995).
[11] J. G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995), and references therein.
[12] Y. Chen, X. W. Lin, Z. Liliental-Weber, J. Washburn, J. Klem, and J. Y. Tsao, Appl. Phys. Lett. **68**, 111 (1996).
[13] X. W. Lin, Z. Liliental-Weber, J. Washburn, E. R. Weber, A. Sasaki, A. Wakahara, and T. Hasegawa, Phys. Rev. B **52**, 16 581 (1995).
[14] C. Ling, J. Math. Phys. **26**, 284 (1948).
[15] M. Neuberger, *Handbook of Electronic Materials* (IFI/Plenum Data Corporation, New York, 1971).
[16] Q. Xie, P. Chen, and A. Madhukar, Appl. Phys. Lett. **65**, 2051 (1994).
[17] S. P. Timoshenko and J. N. Goodier, in *Theory of Elasticity* (McGraw-Hill, Inc., New York, 1972).