PHYSICAL REVIEW B VOLUME 56, NUMBER 4 15 JULY 1997-II

# Critical nuclei shapes in the stress-driven 2D-to-3D transition

K. M. Chen, D. E. Jesson, and S. J. Pennycook
*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6031*

T. Thundat and R. J. Warmack
*Health Sciences Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6123*

(Received 25 September 1996; revised manuscript received 2 June 1997)

We investigate the kinetic pathways to coherent island formation during the stress-driven roughening of strained films, and specifically examine the role of facets during island nucleation. Despite the ubiquitous appearance of {501} facets in the Si-Ge system, we show that for $Ge_{0.5}Si_{0.5}$ strained layers, the initial islanding pathway does not involve discrete {501} facets. A kinetic model based on interacting surface steps is developed, which explains the observed pathway and is consistent with the sensitive dependence of the 2D-3D transition on temperature and the sign of misfit. [S0163-1829(97)50232-3]

The structural transition of a planar thin film to a three-dimensional (3D) island morphology is a critical issue in strained-layer epitaxy. In the classic Stranski-Krastanow growth mode, a 2D wetting layer is followed by the formation of 3D islands which can efficiently relieve misfit strain.[1] This mechanism of strain relaxation is seen in a wide variety of materials systems and is presently receiving considerable attention as a possible means of manufacturing semiconductor quantum dots.[2] Nevertheless, despite the importance of the 2D-to-3D transition,[3–8] our current understanding of the kinetic pathways to 3D islands is still very limited.

In a classical nucleation description of coherent islanding, the critical nucleus geometry is of central importance.[9] The energy of this configuration establishes the number of critical nuclei for the transition and profoundly influences the kinetics. Unfortunately, our knowledge of critical configurations is very limited, as the study of critical nuclei geometries presents a considerable experimental challenge. It has, therefore, become customary to infer the geometry of a critical nucleus from the shapes of stable islands. For example, the ubiquitous appearance of {501} facets in the Si-Ge system[6,10] suggests that the critical nucleus is similarly faceted.[5,7]

In this paper, we present a detailed study of the 2D-3D transition of $Ge_xSi_{1-x}$ strained films. We show that, surprisingly, the nucleation of 3D $Ge_{0.5}Si_{0.5}$ islands does not involve discrete {501} facets. This has important implications for the role of atomic steps in the nucleation kinetics. By incorporating the steps into an islanding model, we demonstrate that the kinetic pathway is consistent with the energetics of interacting steps. In general, pathways involving faceted or stepped critical nuclei may compete and will depend on the relative importance of facet and step energies.

Studies of the strain-induced 2D-3D transition are generally impeded by the inherently high supersaturations associated with far-from-equilibrium growth. To avoid these difficulties, we have utilized a gentle post-deposition anneal process which emulates equilibrium surface conditions. This ensures that island growth closely follows a local minimum-energy pathway. Initially, a thin (2 nm) $Ge_{0.5}Si_{0.5}$ epilayer was grown on Si(100) at a relatively low growth temperature of 400 °C, providing a nominally planar alloy surface. Using *in situ* reflection high-energy electron diffraction (RHEED), we monitor the first appearance of a chevron diffraction pattern indicating the formation of faceted islands at a fixed temperature. The transition is extremely sharp, occurring at around 580 °C. For temperatures below 560 °C, the flat film is *metastable* for anneal times as long as 2 h, whereas islands form within a minute at 590 °C or above. The sample was then quickly quenched to room temperature for *ex situ* atomic force microscopy (AFM) measurements.

To capture the evolution of island formation and growth, use was made of the natural temperature gradient across the sample. A temperature difference of $20\pm5°$ between sample center (hotter region) and edge regions (cooler region) produces a significant variation in number density of stable 3D islands as shown in Fig. 1. The formation of discrete islands and the strong temperature dependence of the 3D island density is consistent with a thermal nucleation process of the 2D-3D transition,[5] in which the critical nucleus geometry plays a central role.

We now focus attention on the critical nucleus geometry for the 3D coherent island nucleation. To investigate this issue, we have analyzed the size and shape distribution of the 3D islands shown in Fig. 1. All the islands tend to align along [100] directions. A typical cross sectional profile of an island is shown in Fig. 2, from which a mean inclination angle $\theta$ of the island faces as well as the island half-base-size $s$ can be determined.[11] The island geometry $(s,\theta)$ data plot, shown in Fig. 3, thus represents a comprehensive map detailing the kinetic pathway to large coherent islands. We find that the measured (mean) inclination angles of the island faces are distributed continuously up to 11.3°, which corresponds to the angle of the {501} facet. Many of these islands are above the critical nucleus size since they survive high-temperature anneals.[12] Although the largest islands tend towards strain stabilized {501} facets,[13] many smaller but stable islands have a pyramidal shape with mean inclination angles significantly below the {501} facetting angle indicated by the vertical line in Fig. 3. The energy barrier for the 2D-to-3D transition, therefore, occurs prior to the formation of {501} facets.

 

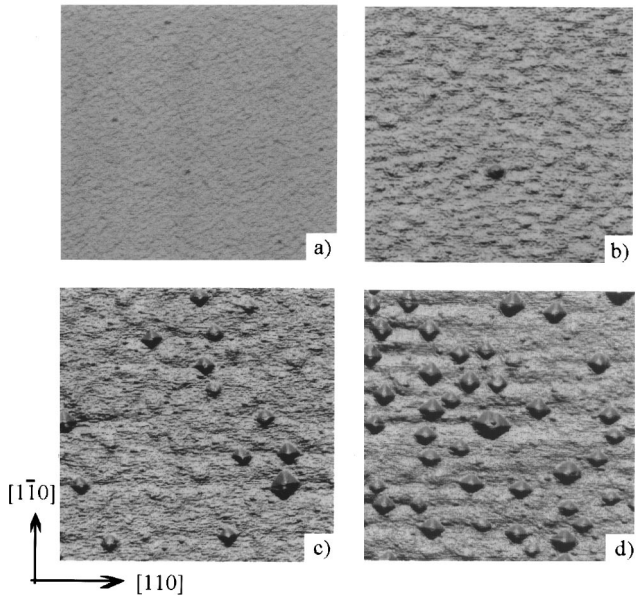


FIG. 1. AFM images of a $Ge_{0.5}Si_{0.5}$ film annealed at (a) 560 °C, (b) 570 °C, (c) 580 °C, and (d) 590 °C for 4 min. The scan size of each image is $1\times1$ $\mu m^2$. The images (b), (c), (d) are taken from different temperature regions of one sample wafer. While the background roughness in (b)–(d) is identical, more numerous and larger pyramidal shaped islands can be seen in the higher temperature regions as a result of island nucleation and growth.

This observation has important implications for the role of surface steps in the island nucleation process. The smallest growing islands are associated with variable small slopes which are microscopically composed of stepped terraces as shown in Fig. 4. The average spacing between neighboring step edges is determined by the mean inclination angle $\theta$ of the surface. In this case, the energetics of the interacting steps, rather than the surface energy of a particular stable facet, will dominate the kinetic pathway of island nucleation. In order to study the physical origin of the pathway, we consider a simple model involving the nucleation and growth of a square-based pyramidal island with stepped surfaces as shown in Fig. 4. The minimum energy pathway for islanding can then be calculated with respect to the varying island size $s$ and inclination of the faces $\theta$.

The free-energy change accompanying the formation of

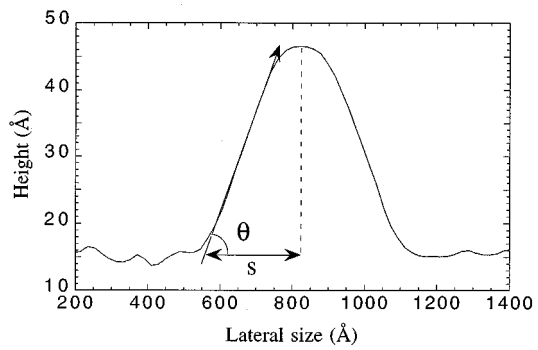


FIG. 2. Cross-sectional AFM line profile of a 3D island. We determine the mean inclination angle $\theta$ by measuring the slope of the arrowed line to avoid the complications due to the tip at the island corners. The half-base size $s$ is also measured as indicated.

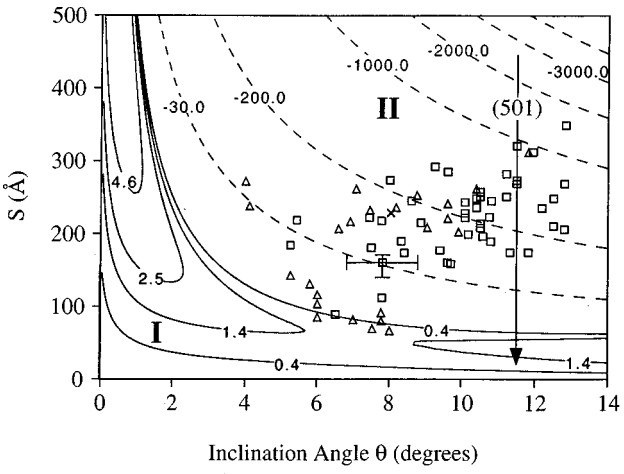


FIG. 3. A distribution of experimentally observed island geometries characterized by half-base size $s$ and inclination angle $\theta$. The crossed, triangular, and square symbols correspond to islands from 1(b), 1(c), and 1(d), respectively. The energy contours $\Delta G(s,\theta)$ in units of eV are fitted to the smallest stable islands, yielding $s_c = 60$ Å and $\theta_c \approx 7°$ (see text). Positive and negative energies are represented by solid and dashed lines, respectively. Parameters used in the calculation are $h = 1.38$ Å, $a = 3.89$ Å, $\mu = 49$ GN m$^{-2}$, $\nu = 0.2$, $\varepsilon = 0.02$, $\lambda_0 = 2.7$ meV/Å, and $\lambda_d = 4.4$ meV/Å.

the 3D island from a planar film is given by $\Delta G = \Delta G_s - \Delta G_r$. The elastic relaxation energy $\Delta G_r$ drives the 3D island formation but is opposed by the cost in surface energy $\Delta G_s$ associated with the creation of steps. Since the island bases preferentially align along the elastically soft [100] directions, the steps are primarily associated with [100]-type monatomic steps. If we neglect terms associated with the corners and treat the steps to have a mean length $s$ (consistent with the treatment of Tersoff *et al.*[5]), the additional cost in surface free energy of a pyramidal island can be written as[14]

$$\Delta G_s = \frac{4s^2 \tan\theta}{h}\left[\lambda_0 + \lambda_d\left(\frac{a}{h\cot\theta}\right)^2\right], \qquad (1)$$

where $\lambda_0$ is the step creation energy per unit length, $h$ and $a$ are the step height and surface lattice constant, respectively. The second term in the bracket represents contributions from repulsive interactions between steps or ''force dipoles.''

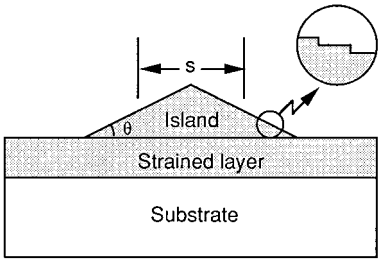


FIG. 4. Cross section of a square-based pyramidal island geometry. The 3D island is considered as a vertical stack of monolayer islands.

The reduction of the strain energy associated with the elastic relaxation of the pyramidal island is given by[5] $\Delta G_r = 6cs^3 \tan^2\theta$. Here $c=\sigma^2(1-\nu)/2\pi\mu$, where $\mu$ and $\nu$ are the shear modulus and Poisson ratio of the substrate and $\sigma$ is the bulk stress of the uniform epilayer. Therefore, the total free energy (change) of a pyramidal stepped island is

$$\Delta G(s,\theta) = -6cs^3 \tan^2\theta + \frac{4s^2 \tan\theta}{h} \times \left[\lambda_0 + \lambda_d \left(\frac{a}{h \cot\theta}\right)^2\right]. \quad (2)$$

A contour map of island energy $\Delta G(s,\theta)$ is plotted against $s$ and $\theta$ in Fig. 3 using Eq. (2). An energy barrier ridge partitions the island geometry into regions I and II. Small or shallow islands in region I must first overcome the energy barrier to access region II and continue to grow. The energy barrier arises because the increase in surface free energy due to step creation initially outweighs the energy gained from elastic relaxation. The two-dimensional energy surface in Fig. 3, therefore, determines the kinetic pathways for island evolution, and the energy ridge provides the crucial rate-limiting step to the observed 2D-3D transition.

It is important to note that a saddle point $(s_c,\theta_c)$ exists in the energy surface corresponding to a minimum energy barrier $\Delta G^*(s_c,\theta_c)$ given by

$$\Delta G^*(s_c,\theta_c) = 2\left(\frac{8\pi}{15}\right)^2 \frac{a\lambda_0^2(1-\nu)^2\sqrt{\lambda_0\lambda_d}}{\sqrt{5}h^4(1+\nu)^4\mu^2\varepsilon^4}, \quad (3)$$

which occurs at

$$\tan\theta_c = (h/a)\sqrt{\lambda_0/5\lambda_d}, \quad (4)$$

and

$$s_c = 8a\sqrt{\lambda_0\lambda_d}/3\sqrt{5}h^2c. \quad (5)$$

The most likely pathways for island nucleation are those passing over the saddle point, which defines both the critical nucleus shape and the maximum rate of island nucleation given by $R \propto \exp(-\Delta G^*(s_c,\theta_c)/kT)$.

Given the uncertainties in the step parameters $\lambda_0$ and $\lambda_d$ and the inherent approximations in the model for strain relaxation,[15] we would not expect our model to quantitatively predict the form of the experimental data in Fig. 3. However, it does describe the important qualitative physics as can be observed by fitting the saddle point to the experimentally observed smallest islands in Fig. 3. Clearly, the evolutionary pathways of the islands are constrained to pass over the saddle point where the activation barrier is a minimum. Once over the saddle point, rapid island growth due to steep gradients in the energy surface, coupled with variations in the local kinetics, produce the observed scatter in island shape and size. Our simple model, based on the energetics of interacting steps, would therefore appear to provide a useful qualitative description of strained island nucleation and growth.

We now discuss the conditions, under which pathways involving {501} faceted nuclei (represented as a vertical line in Fig. 3) may dominate pathways involving nuclei comprised of individual steps. The energy barrier to the facet pathway is $(4\Gamma)^3/3(9c)^2 \tan\theta_0$, where $\Gamma = \gamma_e \csc\theta_0 - \gamma_s \cot\theta_0$, and $\gamma_e$ and $\gamma_s$ are the surface free energy per unit area for the {501} facet and {001} surface, respectively.[5] $\theta_0$ is the inclination angle of the {501} facet, corresponding to 11.3°. Obviously, if the orientational dependence of the surface energy has a deep *cusped* local minimum at {501} facets as a result of misfit strain and atomic reconstruction, the {501} faceted critical nuclei might correspond to a lower energy barrier and thus dominate the island nucleation. Such a condition is fulfilled if the energy barrier for faceted island nucleation is smaller than the energy barrier given by Eq. (3), giving

$$\gamma_e < \gamma_s \cos\theta_0 + 6(a\tan\theta_0)^{1/3} \sin\theta_0 (\lambda_0/5)^{5/6} \lambda_d^{1/6}/h^{4/3}. \quad (6)$$

However, our experimental observation clearly indicates that this is not the case for the $Ge_{0.5}Si_{0.5}$/Si(001) system.

Now consider the dependence of the 2D-3D transition on the misfit (both magnitude and sign) and temperature. The $\varepsilon^{-4}$ functional dependence of the energy barrier in Eq. (3) clearly demonstrates the sensitivity of 3D island nucleation to the magnitude of misfit strain $\varepsilon$. However, strain also influences the step (creation) free energy $\lambda_0$, which causes the barrier to sensitively depend on the *sign* of the strain as well. Recent studies[8,16] have shown that, for Si(001) and Ge(001) $S_B$ and $D_B$ type surface steps, compressive strain reduces the formation energies significantly, whereas tensile strain increases the formation energies. Assuming that similar arguments apply to [100] steps, the activation barrier for the 2D-3D transition [Eq. (3)] would be increased dramatically for epilayers in tension. We have confirmed this by annealing 2 nm $Ge_{0.5}Si_{0.5}$/Ge(100) samples, in which the 2% tensile strained $Ge_{0.5}Si_{0.5}$ films remained planar even after $\geqslant$600 °C annealing.[17] This is consistent with the observation of Xie *et al.*[8] that, as a result of changes in step free energy, tensile-stressed surfaces did not significantly roughen, even during growth at high temperatures.

The step model also qualitatively explains the abruptness of the 2D-3D transition with anneal temperature. It is well known that the step free energy $\lambda_0$ decreases with increasing temperature due to thermal entropy contributions, until it vanishes at the thermal roughening transition.[18] Since $\Delta G^*(s_c,\theta_c)$ is proportional to $\lambda_0^{5/2}$, the barrier is also temperature dependent so that the 3D island nucleation rate $R \propto \exp(-\Delta G^*(s_c,\theta_c)/kT)$ does not follow a simple Arrhenius behavior with a temperature-independent activation energy. This indicates that, at least in part, the abrupt nature of the 2D-3D transition can be attributed to the significant reduction in the energy barrier $\Delta G^*(s_c,\theta_c)$ with increasing temperature. A barrierless 2D-3D transition is expected for the temperatures above the thermal roughening temperature, where the continuum model of morphological instability theory becomes valid.[5]

In summary, we have observed a kinetic pathway of the stress-driven 2D-to-3D transition which does not involve stable facets. Our experimental results demonstrate that the lateral width and inclination angle evolve continuously until eventually the islands are approximately bounded by strain

stabilized {501} facets as indicated by the vertical line in Fig. 3. This shows that, at least for the $Ge_{0.5}Si_{0.5}$ films studied here, the energetics of individual (but elastically interacting) steps is responsible for the observed kinetic pathway to 3D roughening. Surprisingly, the critical nuclei are, therefore, not bounded by discrete {501} facets as might be initially anticipated. The interpretation of this transition in terms of the energetics of individual steps (rather than facets) provides a consistent explanation for the experimentally observed island geometries as well as the temperature and strain (sign) dependence of the transition.

This research was sponsored by the Division of Material Science, U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

[1] D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).

[2] D. Leonard, K. Pond, and P. M. Petroff, Phys. Rev. B **50**, 11 687 (1994).

[3] M. A. Grinfeld, Sov. Phys. Dokl. **31**, 831 (1986); D. J. Srolovitz, Acta Metall. **37**, 621 (1989); H. Gao, Int. J. Solids Struct. **28**, 703 (1991).

[4] B. J. Spencer, P. W. Voorhees, and S. H. Davis, J. Appl. Phys. **73**, 4955 (1993).

[5] J. Tersoff and F. K. LeGoues, Phys. Rev. Lett. **72**, 3570 (1994).

[6] M. A. Lutz *et al.*, Surf. Sci. **316**, L1075 (1994).

[7] J. Tersoff, Phys. Rev. Lett. **74**, 4962 (1995).

[8] Y. H. Xie *et al.*, Phys. Rev. Lett. **73**, 3006 (1994); *ibid.* **74**, 4963 (1995).

[9] J. W. Christian, *The Theory of Transformations of Metals and Alloys*, 2nd ed. (Pergamon, New York, 1975), Part I, p. 418.

[10] Y-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).

[11] The finite size of our AFM tip (radius approximately 10 nm) will influence the measurements of local details at the sharp corners of islands. We therefore avoid such complications by measuring inclination angles away from the island corners. The measured island (half-base) size $s$ is broadened by less than 1 nm due to the tip-island convolution for inclination angles $\leqslant 12°$ [see T. Thundat *et al.*, Scanning Microsc. **6**, 903 (1992)].

[12] Islands of similar geometries were also observed on other $Ge_{0.5}Si_{0.5}$ samples which have been annealed at high temperatures above 600 °C.

[13] Some of the larger islands are associated with flat tops with cross sectional profiles similar to the one in Fig. 2.

[14] T. W. Poon *et al.*,, Phys. Rev. Lett. **65**, 2161 (1990); O. A. Alerhand *et al.*, *ibid.* **61**, 1973 (1988). Since the $(2\times N)$ and $(N\times 2)$ surface stress tensor components are equal along the direction normal to [100] steps, we neglect relaxation effects associated with surface stress anisotropy along $\langle 110\rangle$ directions.

[15] J. Tersoff and R. M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).

[16] K. M. Chen *et al.*, Phys. Rev. Lett. **75**, 1582 (1995).

[17] At even greater temperatures, roughening is associated with defects.

[18] N. C. Bartelt, R. M. Tromp, and E. D. Williams, Phys. Rev. Lett. **73**, 1656 (1994). The roughening temperature for the Si(001) surface was observed to be about 1200 °C, but the entropy effect becomes significant for temperatures above 500 °C. We expect that the roughening temperature for the surface of strained GeSi films is lower than that for the Si(001) due to the weaker atomic bonds and the misfit strain.