

Dislocation-Free Stranski-Krastanow Growth of Ge on Si(100)

D. J. Eaglesham and M. Cerullo

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

(Received 27 December 1989)

We show that the islands formed in Stranski-Krastanow (SK) growth of Ge on Si(100) are initially *dislocation-free*. Island formation in true SK growth should be driven by strain relaxation in large, dislocated islands. Coherent SK growth is explained in terms of *elastic* deformation around the islands, which partially accommodates mismatch. The limiting critical thickness, h_c , of coherent SK islands is shown to be higher than that for 2D growth. We demonstrate growth of dislocation-free Ge islands on Si to a thickness of $\approx 500 \text{ \AA}$, $50\times$ higher than h_c for 2D Ge/Si epitaxy.

PACS numbers: 68.55.Ln

There are three known modes of heteroepitaxial growth:¹ Frank-van der Merwe (FvdM) (Ref. 2), Volmer-Weber (VW) (Ref. 3), and Stranski-Krastanow (SK) (Ref. 4); these may be loosely described as layer-by-layer (2D), island growth (3D), and layer-by-layer plus islands (Fig. 1). All three of these modes have been observed experimentally, for example, in Au/Ag (Ref. 5), Au/molybdenite,⁶ and InAs/GaAs.⁷ A very large number of studies have been devoted to the identification of the precise growth mechanism in different systems. The importance of this problem lies both in establishing the experimental conditions for optimum crystal growth, and in testing the theories that underpin our understanding of the crystal-growth process.

Which growth mode will be adopted in a given system will depend on the interfacial free-energy terms and on the lattice mismatch. In lattice-matched systems, island formation is driven by high interface energy γ_{12} and high epilayer surface energy σ_2 : Islands form provided $\sigma_2 + \gamma_{12} < \sigma_1$, the substrate surface energy. Changes in $\sigma_2 + \gamma_{12}$ can only drive a transition from FvdM to VW: The epilayer either wets the substrate or does not. For a strained epilayer there is the additional possibility that island formation may allow the system to introduce misfit dislocations underneath the islands to relax epi-

layer strain. For a system with small interface energy but large lattice mismatch, initial growth is layer by layer, but a thicker layer has large strain energy and can lower its total energy by forming isolated thick islands in which the strain is relaxed by interfacial misfit dislocations: Thus, SK growth occurs in strained systems.¹

It should be emphasized that these elementary free-energy considerations imply that the primary driving force for island formation in SK growth must be the ability to introduce dislocations in the islands: If surface free energies favored island formation, then the system would grow in VW mode. In this Letter we present evidence that during SK growth of Ge on Si, the islands formed at an early stage of growth are dislocation-free; we shall then attempt to explain this "coherent SK growth," and determine the critical island size for dislocation introduction.

The early stages of growth of Ge/Si have been very extensively studied.⁷⁻¹⁵ As is typical for semiconductor heteroepitaxy, the epilayer has a fairly low interface energy but a substantial lattice mismatch, and SK growth occurs. Early studies used reflection high-energy electron diffraction (RHEED) and optical microscopy^{8,9} to show island formation after $\approx 10 \text{ \AA}$ of growth. MeV ion scattering¹⁰ subsequently revealed that the initial layer is coherent and grows layer by layer, but once islands form the interface is incoherent. Auger experiments¹¹⁻¹³ suggest that the thickness for island formation is ≈ 3 monolayers (ML) of layer-by-layer growth. RHEED-oscillation studies,¹⁴ on the other hand, show six distinct RHEED oscillations occurring during Ge deposition prior to island formation, suggesting 6 ML of Ge prior to island formation, but confirming SK growth. In addition to studies of molecular-beam-epitaxy (MBE) growth conditions, SK growth has also been shown to occur under a variety of experimental conditions, including gas-source growth.¹⁵ Very recent work^{16,17} has succeeded in controlling the transformation from 2D to 3D growth under SK conditions: The authors were able to use a surfactant (As) to suppress island formation, thereby elegantly extending layer-by-layer growth to substantial thicknesses. Here, however, we shall concentrate on the microstructure of Ge islands on Si, as observed in

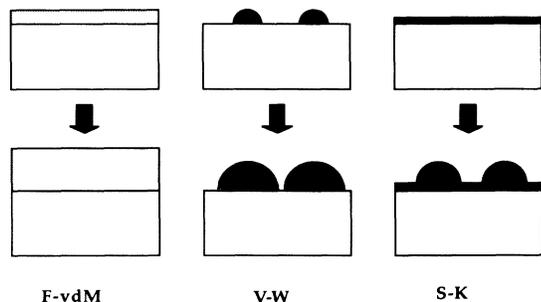


FIG. 1. Schematic diagram of the three possible growth modes: Frank-van der Merwe, Volmer-Weber, and Stranski-Krastanov. Where interface energy alone is sufficient to cause island formation, VW growth will occur; SK growth is uniquely confined to systems where the island strain energy is lowered by misfit dislocations underneath the islands.

transmission electron microscopy (TEM).

Ge/Si epilayers were grown in an MBE chamber with a base pressure of 5×10^{-11} τ using e -gun sources. Substrates were initially cleaned using a modified Shiraki procedure; the Si(100) surface was then prepared by desorbing the thick oxide and growing a thick (0.1–0.5- μm) Si buffer layer. Ge deposition was commenced ≈ 1 s after Si growth was stopped. Figure 2 shows a plan-view TEM sample of a layer on which 8.14 \AA (3 ML) of Ge has been deposited at a growth rate of 0.06 \AA s^{-1} and a deposition temperature of 500°C . (Average coverages were found from Rutherford backscattering, growth rates determined using a calibrated Inficon gauge, and temperatures measured using a pyrometer.) 40-nm-diam islands can be seen under both bright-field and dark-field conditions: Neither show any misfit dislocations. Since we would expect either bright-field or weak-beam images to reveal the presence of any interfa-

cial defects, we conclude that these islands are truly dislocation-free.

As was emphasized earlier, islands form in SK growth in order to reduce the epilayer free energy by relaxing misfit strains with interfacial dislocations: This reasoning is implicit in the earliest discussions of heteroepitaxial growth modes,¹ and has subsequently been made explicit in a number of theoretical studies of islanding.¹⁸ There appear to be only two possible explanations for dislocation-free island formation in Ge/Si epitaxy. The first is that the system is undergoing VW growth: In view of the very large number of experiments which have shown Ge/Si(100) to be an SK system, this does not seem to be likely. The second possibility is that some finite strain relaxation of the islands can occur without misfit-dislocation introduction. A suggestion that this latter process may be occurring can be found in the heavy strain contrast at the islands in Fig. 2, suggesting significant local strain relaxation near an island. A strain field such as that shown schematically in Fig. 3 would relax misfit strain in the island, thereby allowing islanding *without* dislocation introduction (even under SK conditions, i.e., where interface energies alone would dictate layer-by-layer growth); it also accounts for the strain contrast in Fig. 2. It should be noted that a strained island must inevitably produce a deformation similar to that shown in Fig. 3, and that this deformation will bring the island closer to its bulk lattice parameter. We therefore propose that *elastic* deformation of the substrate and the island lowers the strain energy of islands (under all circumstances) and that under certain conditions this strain relaxation will be sufficient to allow coherent Stranski-Krastanow island formation to occur. The energy barrier to coherent island formation is very small (a small increase in surface area or step density), while the formation of relaxed islands requires nucleation of dislocation half loops. Thus coherent SK is-

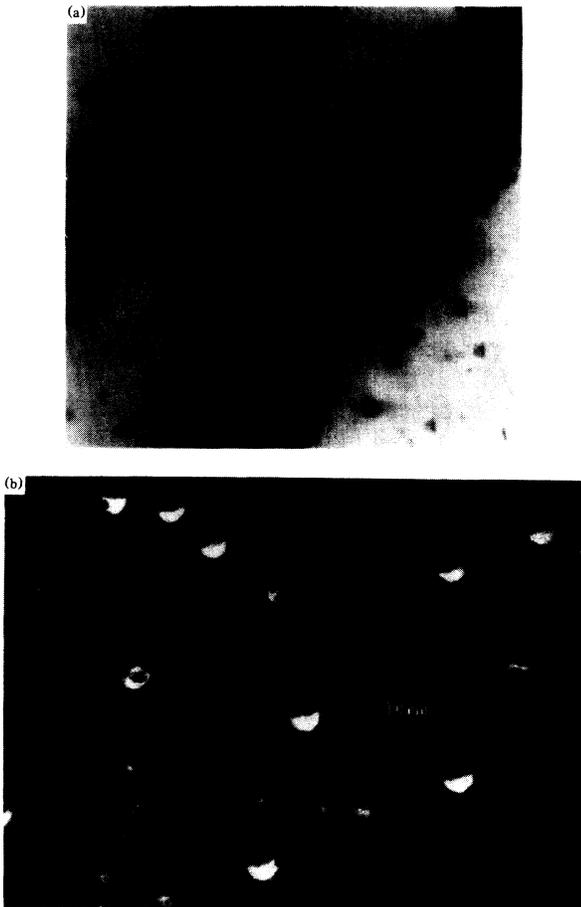


FIG. 2. (a) Bright-field and (b) dark-field plan-view TEM images of Ge islands formed after a 8.14- \AA Ge deposition on a clean Si(100) surface. Both (a) and (b) show the islands to be free of dislocations. Bright-field image at the (022) Bragg position, and (022) dark-field image under $g, 3g$ weak-beam conditions. Note the very heavy strain contrast in both images (easily distinguished from dislocation contrast).

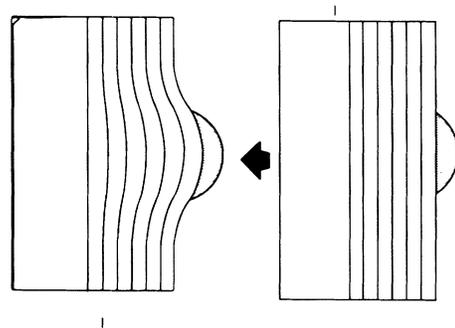


FIG. 3. Schematic showing island strain relaxation by local elastic deformation of near-surface layers in the substrate. This shows how (100) planes can acquire radius of curvature, partially accommodating lattice mismatch and leading to coherent SK growth. Note that this mechanism can only produce significant relaxation of an isolated island; reducing the island spacing will lead to dislocation introduction.

land growth may be local minimum in the free energy of a growing layer that has not yet nucleated true (relaxed) SK islands.

Several previous experiments have examined the strain relaxation of thin films of Ge/Si, and it is appropriate at this stage to address the discrepancies. Various ion-scattering experiments^{10,19} have shown that strain relaxation occurs at $\approx 10 \text{ \AA}$, coinciding with the island formation point, and RHEED-oscillation studies¹⁴ (which provide a very clear indication of the islanding transition) also suggest a change in the in-plane lattice parameter at the same point during growth. However, in a coherent SK island, with the local strain shown in Fig. 3, we would expect both an interface peak, arising due to the bending of planes parallel to $[001]$, and a significant relaxation of the Ge towards its bulk lattice parameter. Finally, recently published¹⁷ TEM images of islands approximately the same size as those in Fig. 2 show evidence of a network of misfit dislocations at the interface. This apparent conflict illustrates the dependence of the strain distributions on island densities, or equivalently on total average coverage. While the islands in Fig. 2 have spacings typically $> 3\times$ their diameter, those in Ref. 17 have spacings approximately equal to their diameter. Coherent islands require substrate deformation over a range $\approx 2\times$ the island diameter: Thus, when the growth conditions give a small island spacing, islands will be relaxed by misfit dislocations instead of substrate strain. This island-spacing dependence will thus produce a transition from coherent SK to true SK growth at some critical coverage.

It remains unclear how widespread coherent SK islanding processes are. Coherent island formation is favored by large barriers to dislocation introduction at large lattice mismatch. Coherent highly strained islands were first reported in early studies of $\beta\text{-Co/Cu}$ epitaxy,²⁰ but it is unclear whether this is an SK or VW system; generally, dislocation introduction is expected at an earlier stage for metal epitaxy than for semiconductors. It also seems unlikely that coherent islands form in large-misfit III-V/III-V heteroepitaxy. However, TEM studies of island formation in GaAs growth on Si have shown that at the earliest stages of growth the islands are coherent.²¹ While this study reported the absence of a monolayer coverage outside the islands, very recent observations of GaAs/Si (Ref. 22) suggest that the growth mode is SK. This may imply a coherent SK island formation in GaAs/Si, although the geometry of GaAs islands on Si dictates that the elastic relaxation must be dominated by deformation of the island, rather than the substrate. (It should be noted, however, that for a polar/nonpolar system such as GaAs/Si the surface and interface free energies depend strongly on the detailed bonding arrangements, so that the discussion given above in the second paragraph is too simplified.)

Finally, we have attempted to use the strain-stabilized islands of coherent SK growth to grow Ge beyond its

“critical thickness” for dislocation introduction.²³ The upper limit for the strain stabilization expected due to substrate deformation is where the nominal strain in the island is equipartitioned between the island and substrate: For Ge/Si islands with this peak relaxation, the epilayer strain is only 2%, and the experimental critical thickness would be expected to increase by a factor of ≈ 10 , from 10 to 100 \AA . We accordingly grew a series of Ge layers of different thicknesses in order to establish the point at which dislocations will be introduced into these partially relaxed islands.

Figure 4 shows a layer close to the point at which dislocations are finally introduced. The islands are $0.14 \mu\text{m}$ in diameter and $> 500 \text{ \AA}$ thick at their peak. (Cross-section TEM provides only a lower limit for thickness, since the sample typically will not pass through the center of the island.) Once islands grow larger than those shown in Fig. 4, near-circular dislocations are introduced concentrically in each island. This represents a fiftyfold increase in critical thickness, and is surprising in view of the maximum strain relaxation dis-

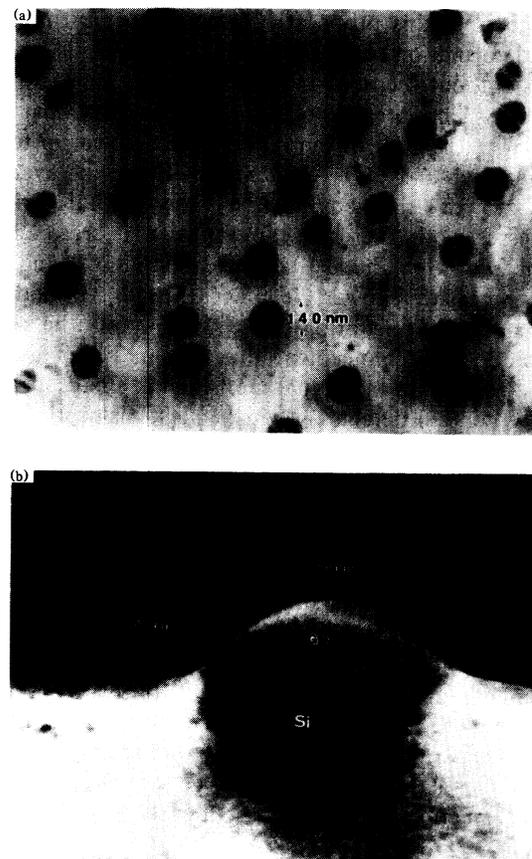


FIG. 4. Plan-view and cross-section TEM images of large coherent SK islands close to their maximum size prior to dislocation introduction. (a) Bright-field image near the $\{202\}$ Bragg position showing characteristic “bend-contour” contrast due to dome-shaped deformation of the substrate around the island. (b) (400) dark-field image; note strong strain contrast around island.

cussed above. The contrast seen in Fig. 4(a) we can interpret, in these larger islands, as the "bend-contour" patterns which are seen in TEM when the crystal is locally bent into a dome shape: The two black lines seen in each island in plan view correspond to the two places where the crystal satisfies the (022) Bragg position. Thus the crystal bends by $2\theta_B(022)$ between the two lines in each island. Knowing $2\theta_B$, we can calculate the radius of curvature $r_c \approx 7 \mu\text{m}$, and thus the degree of strain relaxation due to curvature: For $r_c = 7 \mu\text{m}$, the strain between the surface Ge in a 50-nm island and a Si layer 50 nm below the surface is 1.5%. Thus we would expect to reduce the strain in the Ge islands from 4% to 2.5%. This strain reduction is largely responsible for the fiftyfold increase in the critical thickness in these layers.

It remains unclear whether we can exploit this dislocation-free growth practically. A similar local deformation process, in the islands rather than the substrate, led previous workers²⁴ to propose growth on either 100-Å mesas or porous Si as a way to enhance the critical thickness (the nature of the strains in islands dictates this very short length scale, which has currently limited the success of this proposal). It now appears that substrate deformation may allow us to eliminate misfit dislocations without the need to pattern growth on such a local scale. The present observation suggests that dislocation-free islands of pure Ge can be grown up to 0.1 μm diameter and 500 Å thickness. Since in layer-by-layer growth the equilibrium and actual critical thicknesses both increase rapidly with decreasing Ge content, we might hope that this maximum island size would increase for lower Ge concentrations. In addition to the substrate relaxation effect, we may also be seeing a considerable enhancement due to small-area growth effects:²⁵ Since an individual Ge island is small, it is unlikely to contain defects on which misfit dislocations can nucleate, and can thereby attain an enhanced degree of metastability. Although the metastability mechanism has proved highly successful in reducing misfit-dislocation densities, it is clear that this process alone cannot explain our results, and, in particular, it cannot explain the coherent SK islanding.

We have shown that in SK growth of Ge/Si(100) the Ge islands formed may be dislocation-free. This coherent SK growth arises from local substrate deformation around the island that accommodates an estimated 35% of the strain. We can exploit this strain relaxation to grow Ge islands to a thickness of $> 500 \text{ \AA}$, nearly 2 orders of magnitude above the previously reported exper-

imental critical thickness.

- ¹E. Bauer, Z. Kristallogr. **110**, 372 (1958).
- ²F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. London A **198**, 205 (1949).
- ³M. Volmer and A. Weber, Z. Phys. Chem. **119**, 277 (1926).
- ⁴I. N. Stranski and Von L. Krastanow, Akad. Wiss. Lit. Mainz Math.-Natur. Kl. Iib **146**, 797 (1939).
- ⁵J. W. Matthews, Philos. Mag. **13**, 1207 (1966).
- ⁶D. W. Pashley, M. J. Stowell, M. H. Jacobs, and T. J. Law, Philos. Mag. **10**, 127 (1964).
- ⁷B. Elman, E. S. Koteles, P. Melman, C. Jagannath, J. Lee, and D. Dugger, Appl. Phys. Lett. **55**, 1659 (1989).
- ⁸L. N. Aleksandrov, R. N. Lovyagin, O. P. Pchelyakov, and S. I. Stenin, J. Cryst. Growth **24/25**, 298 (1974).
- ⁹A. G. Cullis and G. R. Booker, J. Cryst. Growth **9**, 132 (1971).
- ¹⁰T. Narusawa and W. M. Gibson, Phys. Rev. Lett. **47**, 1459 (1981).
- ¹¹H.-J. Gossman, L. C. Feldman, and W. M. Gibson, Surf. Sci. **155**, 413 (1985).
- ¹²M. Asai, H. Ueba, and C. Tatsuyama, J. Appl. Phys. **58**, 2577 (1985).
- ¹³K. Kataoka, H. Ueba, and C. Tatsuyama, J. Appl. Phys. **63**, 749 (1988).
- ¹⁴K. Miki, K. Sakamoto, and T. Sakamoto, in *Chemistry and Defects in Semiconductor Heterostructures*, edited by M. Kawabe, E. R. Weber, and R. S. Williams, Proceedings of Symposium D of the 1989 Materials Research Society Meeting (Materials Research Society, Pittsburgh, PA, 1989).
- ¹⁵Y. Koide, S. Zaima, N. Ohshima, and Y. Yasuda, Jpn. J. Appl. Phys. **28**, L690 (1989).
- ¹⁶M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
- ¹⁷F. K. LeGoues, M. Copel, and R. M. Tromp, Phys. Rev. Lett. **63**, 1826 (1989).
- ¹⁸R. Bruinsma and A. Zangwill, Europhys. Lett. **4**, 729 (1987), and references therein.
- ¹⁹J. Bevk, J. P. Mannaerts, L. C. Feldman, B. A. Davidson, and A. Ourmazd, Appl. Phys. Lett. **49**, 286 (1986).
- ²⁰W. A. Jesser and J. W. Matthews, Philos. Mag. **17**, 461 (1968).
- ²¹R. Hull, S. J. Rosner, S. M. Koch, and J. S. Harris, Appl. Phys. Lett. **49**, 1714 (1986).
- ²²D. B. Fenner, D. K. Biegelsen, B. S. Krusor, F. A. Ponce, J. C. Tramontana, M. B. Brooks, and T. W. Sigmon, Appl. Phys. Lett. (to be published).
- ²³R. People and J. C. Bean, Appl. Phys. Lett. **47**, 322 (1985), and references therein.
- ²⁴S. Luryi and E. Suhir, Appl. Phys. Lett. **49**, 140 (1986).
- ²⁵E. A. Fitzgerald, G. P. Watson, R. E. Proano, D. G. Ast, P. D. Kirchner, G. D. Pettit, and J. M. Woodall, J. Appl. Phys. **65**, 220 (1989).

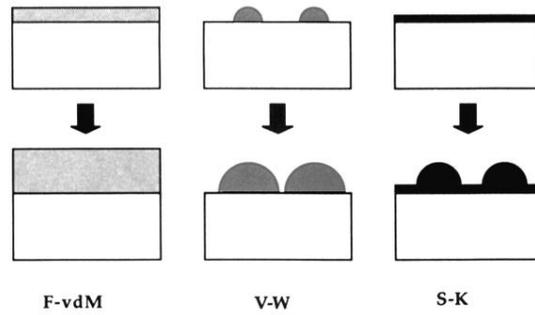


FIG. 1. Schematic diagram of the three possible growth modes: Frank-van der Merwe, Volmer-Weber, and Stranski-Krastinov. Where interface energy alone is sufficient to cause island formation, VW growth will occur; SK growth is uniquely confined to systems where the island strain energy is lowered by misfit dislocations underneath the islands.

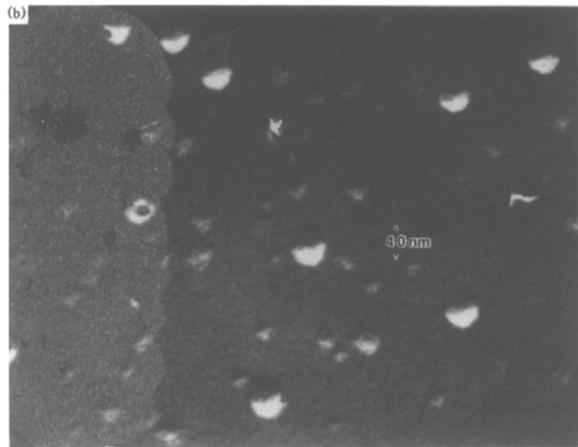
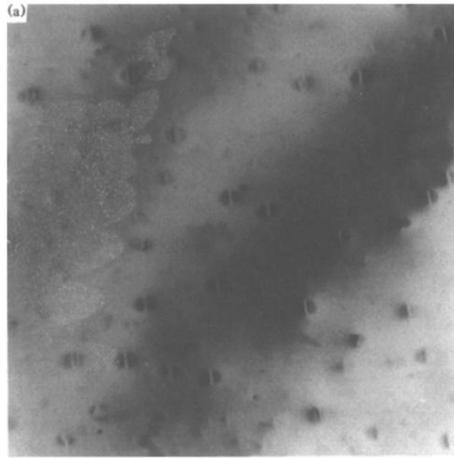


FIG. 2. (a) Bright-field and (b) dark-field plan-view TEM images of Ge islands formed after a 8.14-Å Ge deposition on a clean Si(100) surface. Both (a) and (b) show the islands to be free of dislocations. Bright-field image at the (022) Bragg position, and (022) dark-field image under $g, 3g$ weak-beam conditions. Note the very heavy strain contrast in both images (easily distinguished from dislocation contrast).

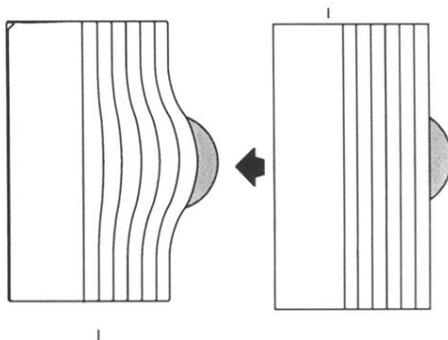


FIG. 3. Schematic showing island strain relaxation by local elastic deformation of near-surface layers in the substrate. This shows how (100) planes can acquire radius of curvature, partially accommodating lattice mismatch and leading to coherent SK growth. Note that this mechanism can only produce significant relaxation of an isolated island; reducing the island spacing will lead to dislocation introduction.

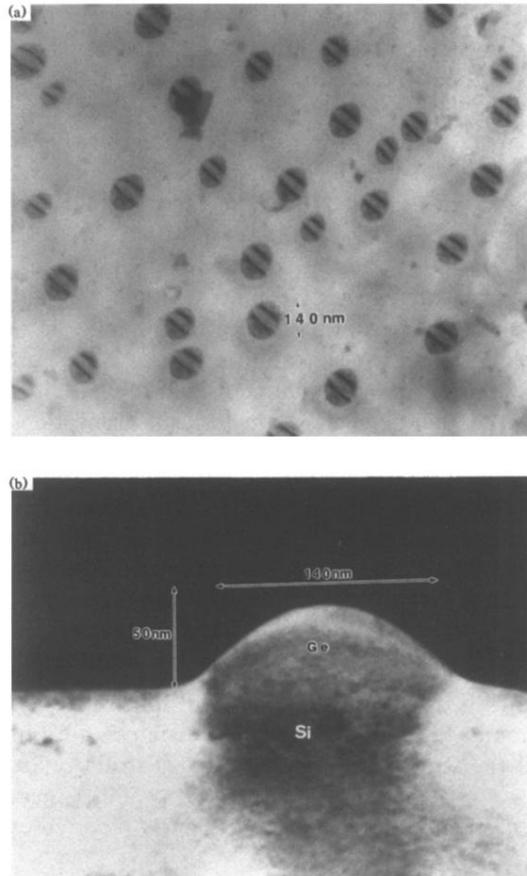


FIG. 4. Plan-view and cross-section TEM images of large coherent SK islands close to their maximum size prior to dislocation introduction. (a) Bright-field image near the $\{202\}$ Bragg position showing characteristic “bend-contour” contrast due to dome-shaped deformation of the substrate around the island. (b) (400) dark-field image; note strong strain contrast around island.