Kinetic Size Selection Mechanisms in Heteroepitaxial Quantum Dot Molecules

J. L. Gray, N. Singh, D. M. Elzey, and R. Hull
Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904-4745 USA

J. A. Floro*
Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, USA
(Received 8 September 2003; published 31 March 2004)

Heteroepitaxial growth of $Si_{0.7}Ge_{0.3}/Si(001)$ films under kinetically limited conditions leads to self-assembly of fourfold quantum dot molecules. These structures obtain a narrowly selected maximum size, independent of film thickness or annealing time. Size selection arises from efficient adatom trapping inside the central pit of the quantum dot molecule when the surrounding islands cojoin to form a continuous wall. Self-limiting growth of nanostructures has significant implications for novel nanoelectronic device architectures such as quantum cellular automata.

DOI: 10.1103/PhysRevLett.92.135504 PACS numbers: 81.07.Ta, 68.35.Fx, 81.15.Hi, 81.16.Dn

Heteroepitaxial strain-layer self-assembly offers a promising approach to the fabrication of quantum nanostructures. The emphasis of research and development is extending from the current focus on strain-driven formation of individual quantum dots to include self-assembly of more complex structures such as quantum dot molecules (QDMs) [1–5]. We showed previously that careful control of growth kinetics during molecular beam epitaxial (MBE) growth of SiGe alloys on Si (001) leads to formation of fourfold symmetric QDMs [3,6–8]. These QDMs form as an inherent result of strain-relieving epilayer growth processes without prior patterning, impurity seeding, or the use of buried stressors. In addition to their scientific interest, QDMs are candidate structures for logic architectures based on quantum cellular automata [9]. In this Letter, we demonstrate that intrinsic QDM structures exhibit a strong tendency to size select via growth stagnation at a specific size, which is a useful property for technological applications. Growth stagnation is quite surprising given the rapid initial growth of these structures and the ample elastic energy available to drive their continued enlargement. We will show that kinetic limitations associated with the loss of easy adatom diffusion pathways as the QDM topology evolves to a closed shape is the likely cause of growth stagnation.

All SiGe films are grown on 1000 Å Si buffers by electron beam evaporation in ultrahigh vacuum onto Shiraki-cleaned Si (001) wafers. Details are given elsewhere [3,10]. MBE growth of $Si_{0.7}Ge_{0.3}$ alloys at temperatures above 700 °C, with relatively low deposition rates of order 0.1 Å/s, leads to the formation of discrete coherent islands that follow a well-known evolutionary sequence [10–14] as a function of mass equivalent thickness: initial growth of a planar wetting layer for the first 10–15 Å, subsequent growth of {105}-faceted pyramids on the wetting layer, transformation of pyramids to multifaceted dome clusters at about 45 Å, and formation of misfit dislocations within dome islands above 100 Å.

Heteroepitaxial growth of $Si_{0.7}Ge_{0.3}/Si$ (001) alloys at lower temperatures and higher deposition rates (here, 550 °C and 0.9 Å/s) dramatically changes morphological evolution [3,7,8]. In this case, the planar wetting layer is kinetically stabilized up to 50 Å thickness. The first 3D morphological evolution that occurs is the formation of shallow pits with sidewall angles 2-4° off {001}, as shown in Fig. 1(a). Pit formation relieves strain in the metastable wetting layer [15]. The ejected material from the pits accumulates around the pit edges via cooperative nucleation [16] to form fourfold QDMs, as shown in Fig. 1(b). With additional deposition, the QDMs enlarge, the walls of the central pit steepen until they facet on {105} planes, and the exterior islands eventually coalesce to form continuous ridges surrounding the pits, as shown in Fig. 1(c). Figure 2 shows that the QDM pits extend at most 60–80 Å below the (001) surface, so most of the SiGe film underneath the QDMs remains metastably strained. This behavior has been observed over a range of process conditions [6], but elevated deposition rate appears to be a prerequisite to QDM formation [3,17]. Previous theoretical work has predicted that high deposition rates will kinetically suppress the roughening instability [18] and can promote preferential formation of pits [19].

Figure 3 shows percentile plots summarizing the size distributions for QDMs in $Si_{0.7}Ge_{0.3}$ films over a range of film thicknesses, with and without annealing at the growth temperature. The data clearly demonstrate that a strongly preferred size exists (about 2200 ± 125 Å), with only minimal enlargement with increasing film thickness, or with annealing at the deposition temperature for 1 h. As shown in Fig. 1(d), further deposition and/or annealing can increase the areal density of QDMs, implying that existing QDMs remain stable while new QDMs nucleate and grow, and stabilize. However, annealing at temperatures only 25 °C higher than the deposition temperature completely destabilizes the QDMs; grooves

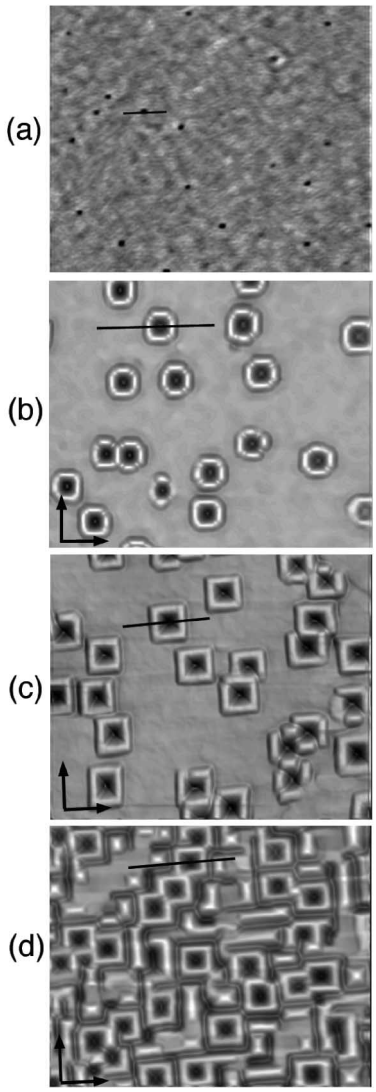

FIG. 1. Atomic force microscope images, 2 μm wide, showing morphology for $Si_{0.7}Ge_{0.3}$ films (a) 50 Å thick; (b) 200 Å thick; (c) 300 Å thick; (d) 300 Å thick annealed for 1 h at 550 °C. Gray scale is optimized for showing edges and is not a true height scale. The arrows show the ⟨100⟩ in-plane directions, and lines indicate where topographic data in Fig. 2 were obtained.

form in the surface that rapidly "bore" down through the metastable wetting layer, forming a dense {105}-faceted island and ridge morphology similar to what would be obtained with higher-temperature deposition [10].

Understanding the origins of size selection by our QDMs is nontrivial. Thermodynamically stable (i.e., noncoarsening) quantum dot sizes have been controversially postulated [13,20]; however, our films are not in a true stable state, as indicated by our higher-temperature annealing results. We have also used 3D finite element (FE) analysis to verify that the elastic strain energy drops monotonically with increasing QDM volume. Thus there is no obvious thermodynamic explanation for the observed QDM stability.

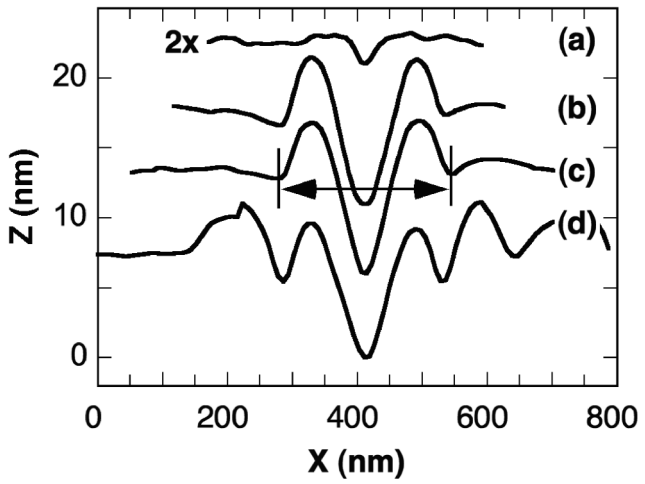

FIG. 2. Line scans of the samples shown in Fig. 1. Traces are offset for clarity. The data for Fig. 1(a) are magnified 2× relative to the other samples. The arrow shows how lateral size of a QDM is defined.

Lacking an energetic stability criterion, QDM size selection must result primarily from kinetic effects. The critical event leading to the growth stagnation of an individual QDM appears to be the near simultaneous formation of continuous ridge surrounding the pit and the emergence of {105} facets. We refer to this structure as a "mature" QDM, differentiated from the structure containing four discrete islands, which we call the "compact" QDM. Since mature QDMs do not enlarge with additional film deposition, they must grow fully conformal, essentially "floating" on the surface of the film as it thickens. *This implies that atoms landing inside the central pit of the QDM are captured efficiently within.* Figure 4 shows 3D FE results for the elastic strain energy distributions for compact and mature QDMs. In the compact structure, adatoms landing in the highly strained pit can diffuse out onto the (001) terrace at the corner regions [see arrows in Fig. 4(a)], where they may then attach to the exterior walls of the islands. This leads to net growth of the QDM. Diffusion from the pit to the exterior of the QDM might also be accomplished along horizontal paths across the island facets as shown in Fig. 4(a). However, when the QDM matures, these diffusion paths are no longer accessible. Adatoms landing in the pit must diffuse up and over the island crest in order to nucleate a new layer on the outer wall and enlarge the QDM [Fig. 4(b)]. However, the crest exhibits the minimum in elastic strain energy, and the interior corner where two ridges meet provides the most favorable location for nucleation of a new facet embryo. This embryo will tend to grow rapidly across the top of the ridge to create a continuous step that subsequent adatoms must cross over in order to escape the pit [see Fig. 4(b)]. If an adatom reaching the resulting step from below has a high probability to attach to the step edge then growth of the interior facet will tend to

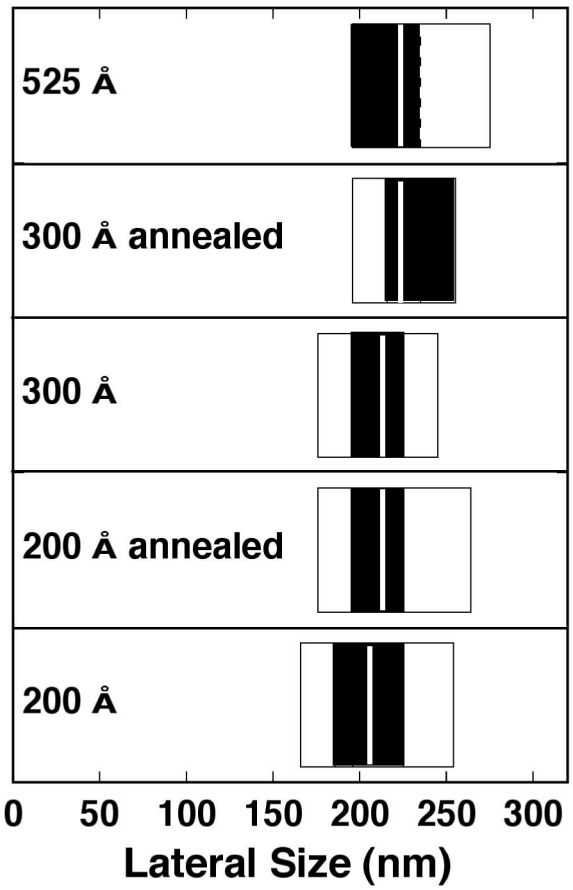

FIG. 3. A percentile plot summary of the size distributions for $Si_{0.7}Ge_{0.3}$ films of different thicknesses, with and without 1 h anneals. Each open box encloses the inner 90% of the data, each filled box encloses the inner 50% of the data, and the white bar represents the mean. For each sample, between 39–45 islands were measured.

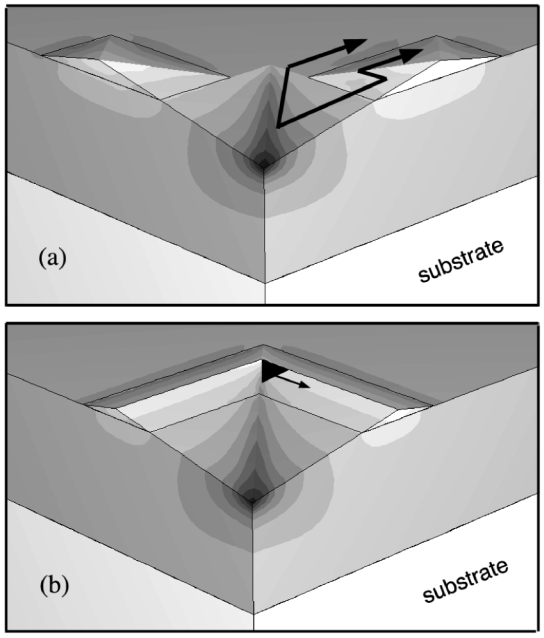

FIG. 4. Results of finite element calculations for (a) compact QDMs and (b) mature QDMs, showing contours of elastic strain energy. The perspective view shows one-fourth of the structure. Lighter shadings represent lower energy, and the darkest contour represents $5.81 \times 10^{+11}$ J/m^3. In (a) the arrows illustrate easy diffusion paths enabling QDM enlargement, while in (b) the triangle and arrow show the optimal facet nucleation and growth process.

complete, promoting conformal growth even though this raises the elastic strain energy of the system. Unfortunately, although better understanding of the Ge {105} surface structure is emerging [21–24], activation barriers for adatom diffusion and step attachment have not to our knowledge been determined, forestalling quantitative evaluation of our model.

We considered several other potential explanations for the sudden suppression of QDM growth rate. Prominent among these are (1) strongly reduced surface diffusivity when {105} facets form at QDM maturation [25] and (2) size-dependent facet nucleation barriers [26]. We tentatively reject (1) since the large, extraordinarily smooth facets obtained during epitaxial growth of Ge on Si (015) suggest that diffusion is fairly rapid at standard growth temperatures [21,27]. Low diffusivity should lead to significant roughening of the {105} facets during deposition, which is not observed. We reject (2) more readily, since conformal propagation of QDMs during deposition directly implies that facet nucleation and growth on the {105} facets must be occurring efficiently under these conditions, even in the presence of strain gradients.

We have demonstrated how growth kinetics can be manipulated to self-assemble fourfold quantum dot molecules that are size selected. These growth studies provide further insight into the local processes associated with strain-induced self-assembly in heterolayers, and the resulting QDM structures are potentially of importance in fabrication of novel quantum electronic architectures.

The authors acknowledge helpful discussions with J. Tersoff, F. Ross, R. Tromp, B. Swartzentruber, J. Bean, P. Kumar, and T. Vandervelde. This work was partially supported by NSF-DMR (Grant No. 0075116) under the UVA-UIUC-IBM-Sandia Focused Research Group "Nanoscale Morphological Evolution of Semiconductor Surfaces," by the NSF Materials Research Science and Engineering Center at the University of Virginia, "The Center for Nanoscopic Materials Design," and by the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory of the United States Department of Energy operated by Sandia Corporation, a Lockheed Martin Company, under Contract No. DE-AC04-94AL85000.

*Electronic address: jafloro@sandia.gov

[1] X. Deng and M. Krishnamurthy, Phys. Rev. Lett. **81**, 1473 (1998).
[2] Y. Zhang, M. Floyd, and J. Drucker, J. Appl. Phys. **90**, 4748 (2001).
[3] J. L. Gray, R. Hull, and J. A. Floro, Appl. Phys. Lett. **81**, 2445 (2002).
[4] G. Cappellini, M. De Seta, C. Spinella, and F. Evangelisti, Appl. Phys. Lett. **82**, 1772 (2003).
[5] M. Borgstrom, V. Zela, and W. Seifert, Nanotechnology **14**, 264 (2003).
[6] T. E. Vandervelde, P. Kumar, T. Kobayashi, J. L. Gray, T. Pernell, J. A. Floro, R. Hull, and J. C. Bean, Appl. Phys. Lett. **83**, 5205 (2003).
[7] R. Hull, J. Gray, C. C. Wu, S. Atha, and J. A. Floro, J. Phys. Condens. Matter **14**, 12 829 (2002).
[8] R. Hull, J. L. Gray, M. Kammler, T. Vandervelde, T. Kobayashi, P. Kumar, T. Pernell, J. C. Bean, J. A. Floro, and F. M. Ross, Mater. Sci. Eng. B **101**, 1 (2003).
[9] G. Bernstein, C. Bazan, M. Chen, C. S. Lent, J. L. Merz, A. O. Orlov, W. Porod, G. L. Snider, and P. D. Tougaw, Superlattices Microstruct. **20**, 447 (1996).
[10] J. A. Floro, E. Chason, L. B. Freund, R. D. Twesten, and R. Q. Hwang, Phys. Rev. B **59**, 1990 (1999).
[11] J. A. Floro, E. Chason, R. D. Twesten, R. Q. Hwang, and L. B. Freund, Phys. Rev. Lett. **79**, 3946 (1997).
[12] M. Tomitori, K. Watanabe, M. Kobayashi, and O. Nishikawa, Appl. Surf. Sci. **76/77**, 322 (1994).
[13] Gilberto Medeiros-Ribeiro, Alexander M. Bratkovski, Theodore I. Kamins, Douglas A. A. Ohlberg, and R. Stanley Williams, Science **279**, 353 (1998).
[14] A. Rastelli and H. von Kanel, Surf. Sci. **532**, 769 (2003).
[15] J. Tersoff and F. Le Goues, Phys. Rev. Lett. **72**, 3570 (1994).
[16] D. E. Jesson, K. M. Chen, S. J. Pennycook, T. Thundat, and R. J. Warmack, Phys. Rev. Lett. **77**, 1330 (1996).
[17] Of course, the more fundamental parameter is the adatom migration length, which (very crudely) is controlled by the deposition rate when the time to deposit a monolayer is much less than the time needed for an adatom to access the natural lateral length scale of the strained system.
[18] B. J. Spencer, P. W. Voorhees, and S. H. Davis, J. Appl. Phys. **73**, 4955 (1993).
[19] C-H. Lam, C-.K Lee, and L. M. Sander, Phys. Rev. Lett. **89**, 216102 (2002).
[20] V. A. Shchukin, N. N. Ledentsov, P. S. Kop'ev, and D. Bimberg, Phys. Rev. Lett. **75**, 2968 (1995).
[21] V. B. Shenoy, C. V. Ciobanu, and L. B. Freund, Appl. Phys. Lett. **81**, 364 (2002).
[22] V. B. Shenoy and L. B. Freund, J. Mech. Phys. Solids **50**, 1817 (2002).
[23] P. Raiteri, D. B. Migas, L. Miglio, A. Rastelli, and H. von Kanel, Phys. Rev. Lett. **88**, 256103 (2002).
[24] Y. Fujikawa, K. Akiyama, T. Nagao, T. Sakurai, M. G. Lagally, T. Hashimoto, Y. Morikawa, and K. Terakura, Phys. Rev. Lett. **88**, 176101 (2002).
[25] J. Tersoff (private communication).
[26] D. Jesson, G. Chen, K. M. Chen, and S. J. Pennycook, Phys. Rev. Lett. **80**, 5156 (1998).
[27] M. Tomitori, K. Watanabe, M. Kobayashi, F. Iwawaki, and O. Nishikawa, Surf. Sci. **301**, 214 (1994).