Molecular Dynamics Study of Coherent Island Energetics, Stresses, and Strains in Highly Strained Epitaxy

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The behavior of energetics, atomically resolved stress, and strain in coherent three-dimensional islands observed in highly strained semiconductor heteroepitaxy is examined for the first time via a molecular dynamics study of a model Ge/Si system. Evidence is found for the common but hitherto unsubstantiated practice of representing the island energy as a sum of surfacelike and bulklike terms, down to rather small islands, but with significantly renormalized coefficients indicating marked modifications of the surface and volume elastic energies commonly employed in continuum descriptions. [S0031-9007(97)03704-6]

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Since the observation of the existence of coherent three-dimensional (3D) islands in the highly strained heteroepitaxical systems InGaAs on GaAs(001) [1] and SiGe on Si(001) [2], interest has rapidly grown in gaining a deeper understanding of the nature of such coherent island formation, their energetics, and the behavior of the stress and strain fields. *Ex situ* and *in situ*, ultrahigh vacuum scanning tunneling microscope (STM) and atomic force microscope (AFM) studies of island size distribution evolution [3–6] and, in some cases, island shape [7,8] have been reported. The strain fields are being examined within the continuum theory of elasticity with the aid of the finite element (FE) methods [9,10]. Recently, the usefulness of such an approach has been examined via comparison between plan-view transmission electron microscope determined image contrast for InAs islands on GaAs(001) and that calculated on the basis of the FE determined strain fields [10]. The strain fields so determined have been compared with those obtained from valence force field calculations [10]. The energetics of the islands have invariably been described under (a) assumed partitioning of the island energy between a surfacelike and a bulklike term and (b) assumed applicability of the continuum theory of elasticity. A recent study has examined [11] the energetics of the equilibrium shape of the InAs 3D islands as a function of its size by combining first-principles calculated surface energies for planes assumed to form the island facets (but neglecting the strain dependence of the surface energy) and the continuum theory based FE approach for the elastic strain energy of the island/substrate system. The significance of the lattice mismatch induced modification of the surface energy of island facets has, however, been demonstrated [12] in earlier analytical descriptions of island energetics based upon continuum theory. A variety of issues pertaining to the significance of the discrete atomic nature to the validity of the above noted assumptions for describing the energetics, and to the kinetics of island formation, shape evolution, the inhomogeneous nature of the spatially resolved strains and stresses, their impact on defect initiation, etc., need to be examined. A molecular dynamics approach allows examination of such issues. Accordingly, in this Letter we report on some results of the first molecular dynamics based examination of a coherently strained island/substrate system. Results are presented on the energetics, atomically resolved stress, and the attendant strain in the Ge islands on the Si(001) system represented in terms of Stillinger-Weber (SW) potentials for Si [13] and Ge [14]. The results reported are of a generic nature and thus of value to island formation in other combinations of materials as well.

The inset in Fig. 1 shows a schematic cross-sectional view of a Ge island with ⟨100⟩ oriented square base and {105} sidewalls (as determined by STM in Ref. [7]) on a Ge wetting layer on Si(001) substrate and the symbols used to

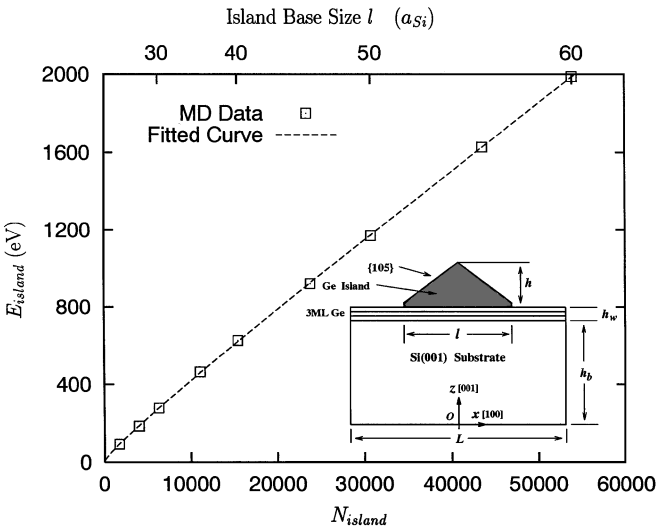

FIG. 1. Island energy (open squares) as a function of N_{island}, the number of Ge atoms in the island, as well as the island base size l in unit of bulk Si lattice constant $a_{\text{Si}} = 5.431$ Å. The broken line is a fit of the form $(aN_{\text{island}}^{2/3} + bN_{\text{island}} + c)$. The inset shows a schematic of the Ge island/Ge wetting layer/Si(001) substrate.

denote the various characteristic parameters of the system. Periodic boundary conditions are applied to the simulation cell of size $L = 434.4$ Å in the x and y directions. The Ge wetting layer thickness (h_w) is held constant at 3 ML as indicated by the experiments and the island base length (l) and height (h) are varied from $l = 108$ Å, $h = 7$ ML to $l = 326$ Å, $h = 23$ ML while keeping the sidewalls the same (i.e., {105}). The total number of Ge atoms in the island, N_{island} (defined here not including the atoms in the wetting layer region below the island base), thus ranged from 1734 to 53 942. Including the atoms of the wetting layer and Si substrate to depths of up to 98 atomic layers, the total number of atoms allowed to follow molecular dynamics correspondingly ranged from $\sim 1.29 \times 10^6$ to $\sim 1.35 \times 10^6$ atoms. Conjugate gradient energy minimization is employed to obtain a locally stable state such that the net force on each atom is less than 10^{-4} eV/Å. For such stable configurations the energies, stresses, and strains are calculated. The atomic level stress components are calculated utilizing the following expression [15]:

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}\left[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4}\sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta)\right], \tag{1}$$

in which $(\alpha, \beta) \equiv (x, y, z)$, m_i and $\vec{p}_i$ are the mass and momentum of atom i, $\vec{r}_{ij}$ is the distance from atom i to j, $\vec{f}_{ij}$ is the force on atom i due to j, and Ω_0 is the average atomic volume.

In Fig. 1 is shown the behavior of the island energy as a function of the number of atoms in the island. Here E_{island} is defined as

$$E_{\text{island}} = E(\text{WL} + \text{3D}) - E(\text{WL}) - N_{\text{island}}\epsilon_{\text{Ge}}, \tag{2}$$

where $E(\text{WL} + \text{3D})$ is the energy of the fully relaxed state of the 3D island with {105} sidewall atoms rebonded on a 3 ML Ge wetting layer having (2×1) reconstruction on Si substrate as shown in the inset, $E(\text{WL})$ is the energy of a system with no island but only the 3 ML thick (2×1) Ge wetting layer relaxed to its own lowest energy state, and ϵ_{Ge} is the cohesive energy per atom of the bulk SW Ge. The E_{island} so defined is thus not simply the energy of the atoms in the geometrically defined island part, but rather accounts also for the changes in energy associated with the atoms in the wetting layer and the Si substrate affected most by the presence of the atoms in the geometrically defined island. Clearly, the synergetic nature of the particle interaction behavior does not allow a clean conceptual separation or partitioning of energies among particles, but the E_{island} as defined here appears to have appeal as it represents mainly the strain and surface energy due to the existence of the island. Hence E_{island} is the mathematical construct that we expect will come closest to the concepts of bulk (volume) strain elastic energy and surface energy traditionally employed in assumed partitioning of the island energy in macroscopic thermodynamic descriptions of island energetics in terms of the continuum theory of solids [9–12]. The dashed line going through the calculated energies represents the functional form [16]

$$\begin{aligned} E_{\text{island}} &= aN_{\text{island}}^{2/3} + bN_{\text{island}} + c, \\ &= a'V_{\text{island}}^{2/3} + b'V_{\text{island}} + c, \end{aligned} \tag{3}$$

in which $a = 0.2133$ eV, $b = 0.0310$ eV, and $c = 8.30$ eV; $V_{\text{island}} = \frac{1}{8}N_{\text{island}}a_{\text{Ge}}^3$ where $a_{\text{Ge}} = 5.659$ Å is the bulk Ge lattice constant; $a' = 26.6$ meV/Å^2, and $b' = 0.17$ meV/Å^3. Remarkably, the excellent fit provides evidence for the first time that the functional form of the total island energy can indeed be well represented by a sum of a surfacelike contribution and a volumelike contribution, hitherto and unsubstantiated assumption in continuum theory based analyses, even down to rather small sized islands. (Note that the smallest size in Fig. 1 is a base of 107 Å, i.e., $20a_0$ wide where a_0 is the Si conventional lattice constant, and 7 atomic layers high.) The presence of the constant c in Eq. (3) indicates that, as expected, at some sufficiently small island size the expression will no longer be adequate. The results also show, however, that the coefficients of the surface and volumelike energy contributions cannot be reliably given by the continuum elasticity theory descriptions. The value a' is markedly smaller than the surface energy of the SW Ge(001) 2×1 surface (~ 80 meV/Å^2), which is also a good estimate of the (105) surface due to the rebonded (2×1) nature of this surface [7]. Likewise, the value of b' is also significantly smaller than the range 0.8 to 1.5 meV/Å^3 obtained from the continuum theory based expressions in Ref. [12], using the relevant elastic coefficients of the SW Ge. The significant renormalization of the coefficients a' and b' is, as anticipated in Ref. [12], a consequence of the relaxation of atoms of the island (including surface reconstruction and rebonding), the wetting layer, and the substrate.

Next, we discuss the behavior of the atomically resolved stress and strain distributions. In Fig. 2 we show the atomically resolved hydrostatic stress, $p_\sigma = \text{Tr}(\sigma_{\alpha\beta})$, along z at $x = 0$, $y = 0$ (i.e., along the vertical line passing through the island base center and apex) for an island with $l = 326$ Å and $h = 23$ ML. The strain components $\varepsilon_{xx} = \Delta a_{[100]}/a_0$ and $\varepsilon_{zz} = \Delta a_{[001]}/a_0$, where a_0 is the bulk lattice constant of Si and Ge in the Si and Ge regions, respectively, are also shown. The behavior of the strain component $\varepsilon_{yy} = \Delta a_{[010]}/a_0$ is very close to ε_{xx}. Note the tensile and long ranged nature of the decay of the hydrostatic stress and the strain components ε_{xx} (and ε_{yy}) into the Si substrate. The ε_{zz} component in this region is seen to be compressive at the interface and then cross over to tensile behavior before decaying to zero. The stress p_σ changes abruptly and dramatically from tensile to compressive over the three Ge atomic layers constituting the wetting layer,

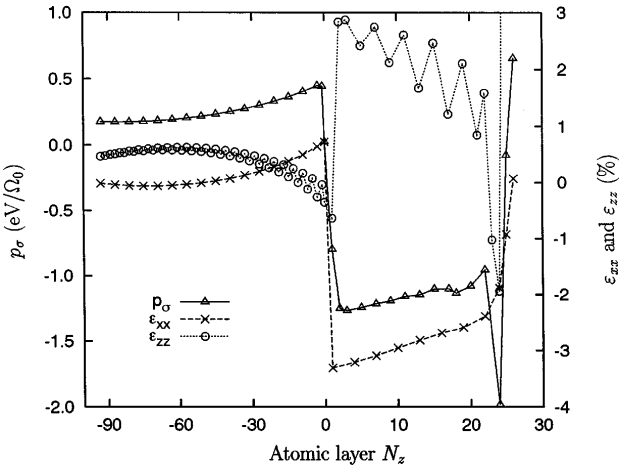

FIG. 2. The hydrostatic stress p_σ and the strain components ε_{xx} and ε_{zz} along z for a line passing through the island apex. $N_z = 0$ denotes the uppermost Si atomic plane. For clarity, the scale for positive N_z values is expanded.

going through near zero at the topmost Si atomic plane ($N_z = 0$) and reaching a maximum value of -1.27 (eV/Ω_0) (i.e., 10.2 GPa) in the third Ge atomic plane. Correspondingly, the strain components ε_{xx}, ε_{yy}, and ε_{zz} also show an abrupt change, including reversal in sign across this boundary. Continuing up into the island towards its apex, the compressive p_σ as well as the strain components are seen to decrease in conformity with expected strain relaxation until we reach within a few atomic layers of the 3D island top. In this region, the influence of the specific geometry of the surface atoms on the top and the {105} sidewalls in terms of surface atom rebonding and reconstruction manifests itself in impacting subsurface stresses and strains. This feature is inherently absent in continuum elasticity theory and hence the finite element analyses of stress and strain at and near the island surface region (i.e., island top and sidewalls). Thus, while the continuum elasticity theory may be adequate for considerations of elastic energies of islands, the above results reveal that for the kinetics of island growth and shape stability the atomistic nature of the islands must explicitly be dealt with [15,17].

Finally, we turn to the morphology of the atomic layers under the island and the (x, y) spatial dependence of the hydrostatic stress p_σ for various atomic planes. In Fig. 3 we show the z position of the atoms along the [100] direction in the topmost Si substrate layer ($N_z = 0$, whose ideal bulk atomic plane is taken as $z = 0$ in these plots) and the fourth Ge atomic layer ($N_z = 4$) from the Si substrate, i.e., the first Ge layer of the 3D island. For an ideal bulk Ge, this layer would be 5.83 Å from the Si atomic layer $N_z = 0$. Plotted are sections along two [100] lines, one passing through the island base center and another along the island edge atoms at the base. Note the curved profile through the center reaching a maximum outward displacement of ~0.6 Å at the center of the Si

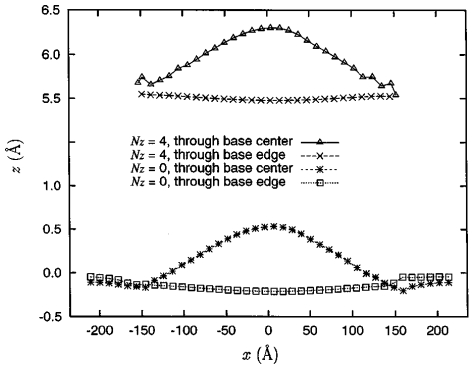

FIG. 3. The z-position profile of the Ge atoms of the first Ge atomic layer of the island ($N_z = 4$) and the uppermost Si substrate atomic layer ($N_z = 0$) along the x direction for atoms on a line passing through the base center and another at the island edge.

($N_z = 0$) and Ge ($N_z = 4$) atomic planes and essentially flat profile at the island edge. The behavior of the corresponding hydrostatic stress p_σ is plotted in Fig. 4. Note the highly compressive and spatially varying nature of p_σ on the first Ge island atomic layer ($N_z = 4$) through the center of the island. By contrast, at the island edge, p_σ is highly tensile and essentially uniform along the edge. Interestingly, the Si substrate topmost atomic layer ($N_z = 0$) is seen to exhibit *compressive* hydrostatic stress along the island center line as well as along the edge. The former shows spatial variation and reaches almost zero near the island center, whereas the latter is essentially uniform. The near zero hydrostatic stress at the center of the Si atomic plane ($N_z = 0$) is accompanied by ~0.6 Å upwards displacement of the atoms (see Fig. 3).

In conclusion, results of the first molecular dynamics examination of the energetics, and atomically resolved stresses and strains in coherent 3D islands on a substrate are presented utilizing the Ge on Si(001) system represented by the Stillinger-Weber potentials as a model vehicle. Analysis of the island energy as a function of size

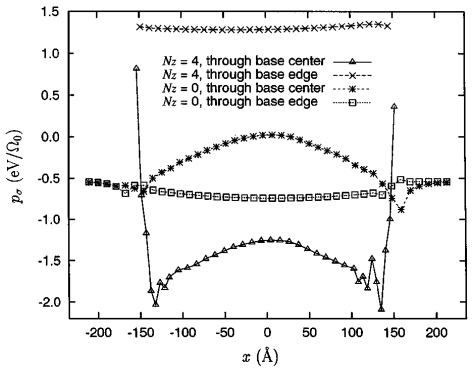

FIG. 4. The x dependence of the hydrostatic stress p_σ for the first atomic layer of the Ge island ($N_z = 4$) and the uppermost Si substrate atomic layer ($N_z = 0$) along lines passing through the island base center and along the edge.

reveals that a functional form comprising a surfacelike and a bulklike term can represent the energy remarkably well down to rather small island sizes. While this provides the first clear justification for the use of such a functional form in continuum theory approaches, the MD results also show that (i) quantitative reliability of the energetics can be seriously compromised by the use of the usual coefficients for surface and bulk elastic energy contributions employed in continuum theories, and (ii) the behavior during growth of islands (such as the mechanism of the island initiation, size and shape evolution, the observed loss of atoms from island edges at early stages [6], etc) is unlikely to be adequately understood within the framework of macroscopic theories utilizing continuum elasticity theory, given the highly inhomogeneous nature of the stresses and strains on an atomic scale. It is hoped that the results presented here will serve as a starting point for examinations of the kinetics of island growth via judiciously chosen simulations.

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[1] S. Guha, A. Madhukar, and K. C. Rajkumar, Appl. Phys. Lett. **57**, 2110 (1990).

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

[3] J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatal, Appl. Phys. Lett. **64**, 196 (1994).

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

[5] Q. Xie, P. Chen, A. Kalburge, T. R. Ramachandran, A. Nayfonov, A. Konkar, and A. Madhukar, J. Cryst. Growth **150**, 357 (1995), and references therein.

[6] N. P. Kobayashi, T. R. Ramachandran, P. Chen, and A. Madhukar, Appl. Phys. Lett. **68**, 3299 (1996); T. R. Ramachandran, R. Heitz, N. P. Kobayashi, A. Kalburge, W. Yu, P. Chen, and A. Madhukar, J. Cryst. Growth (to be published).

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

[8] J. M. Gerard, J. B. Genin, J. Lefebvre, J. M. Moison, N. Lebouche, and F. Barthe, J. Cryst. Growth **150**, 351 (1995).

[9] S. Christiansen, M. Albrecht, H. P. Strunk, and H. J. Maier, Appl. Phys. Lett. **64**, 3617 (1994); S. Christiansen, M. Albrecht, H. P. Strunk, P. O. Hansson, and E. Bauser, Appl. Phys. Lett. **66**, 574 (1995).

[10] T. Benabbas, P. François, Y. Androussi, and A. Lefebvre, J. Appl. Phys. **80**, 2763 (1996).

[11] E. Pehlke, N. Moll, and M. Scheffler, in *Proceedings of the 23rd International Conference on Physics of Semiconductors, Berlin, 1996*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 2, p. 1301.

[12] V. A. Shchukin, N. N. Ledentsov, P. S. Kop'ev, and D. Bimberg, Phys. Rev. Lett. **75**, 2698 (1995).

[13] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[14] K. Ding and C. Anderson, Phys. Rev. B **34**, 6987 (1986).

[15] W. Yu and A. Madhukar, in Ref. [11], Vol. 2, p. 1309.

[16] An edgelike term is omitted from the fitted functional form since, on the atomic scale, the {105} sidewalls of the island are, in fact, made of a train of monoatomic steps separated by $1.25a_0$. Each step edge of the sidewalls thus makes a similar contribution to the total island energy as the one final step edge at the base of the island. Since the total step edge length on the island sidewalls is proportional to $N_{\text{island}}^{2/3}$, the "edge" term in our case is simply a part of the surfacelike term in Eq. (3). Furthermore, from a purely fitting viewpoint, inclusion of a term $(dN_{\text{island}}^{1/3})$, we find, gives a good fit only for rather unphysical values of the constants a, c, and d.

[17] A. Madhukar *et al.*, *Low Dimensional Structures Prepared by Epitaxial Growth or Regrowth on Patterned Substrates*, NATO ASI, Ser. E, Vol. 279 (Kluwer Academic Publishers, The Netherlands, 1995), pp. 19–33.