Evolution of Thermodynamic Potentials in Closed and Open Nanocrystalline Systems: Ge-Si:Si(001) Islands

Marina S. Leite,[1,2] A. Malachias,[1] S. W. Kycia,[3] T. I. Kamins,[4] R. Stanley Williams,[4] and G. Medeiros-Ribeiro[1,4,*]

[1]*Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192 - CEP 13084-971, Campinas, SP, Brazil*

[2]*Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, CP 6165, 13083-970, Campinas, SP, Brazil*

[3]*Department of Physics, MacNaughton Building, Gordon Street, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

[4]*Hewlett-Packard Laboratories, 1501 Page Mill Road, 94304 Palo Alto, California, USA*

(Received 12 December 2007; published 5 June 2008)

An open (closed) system, in which matter is (not) exchanged through surface diffusion, was realized via growth kinetics. Epitaxially grown Si-Ge:Si (001) islands were annealed in different environments affecting the diffusivity of Si adatoms selectively. The evolution of the driving forces for intermixing while approaching the equilibrium was inferred from Synchrotron x-ray measurements of composition and strain. For the open system, intermixing due to the Si inflow from the wetting layer (reservoir) caused a decrease in the Ge content, leading to a lowering of the elastic energy and an increase in the mixing entropy. In contrast, for the closed system, while keeping the average Ge composition constant, atom rearrangement within the islands led to an increase in both elastic and entropic contributions. The Gibbs free energy decreased in both cases, despite the different evolution paths for the composition profiles.

DOI: 10.1103/PhysRevLett.100.226101 PACS numbers: 68.35.Md, 61.66.Dk, 66.30.Pa, 81.10.Aj

Alloying is a process with widespread applications, ranging from metallurgy to electronics. For metals, one can create stronger materials, and for semiconductors, the electronic structure can be tuned, enabling band-gap engineering. The stability of alloys is therefore an issue of intense investigation, as only a few elements form stable solid solutions with each other over wide composition and temperature ranges. The mixing enthalpy will dictate the tendency for forming nonideal solutions. For finite and positive enthalpy, segregation, clustering, Ostwald ripening in binary mixtures, and phase separation are phenomena that can occur as the system approaches the thermodynamic equilibrium [1,2]. What happens to alloys in small systems and what kind of equilibrium structures prevail in the nanoscale regime are still open questions.

A widely studied system is Si-Ge, because of its direct impact on the semiconductor industry. Si-Ge forms an alloy that behaves almost like an ideal mixture, given its small positive enthalpy of solution [1]. Another interesting aspect of the Si-Ge system is the strained epitaxial growth leading to crystalline islands, phenomenon that can be mapped onto other materials systems [3]. These nanostructures can be grown with a high degree of uniformity over large areas, which allows an assessment of statistically meaningful data. Thus, Si-Ge represents an attractive system to investigate alloying at the nanoscale.

The elastic strain energy stored within the island-substrate system is significant, yet smaller than in a 2D pseudomorphic Ge film [4]. For relatively low growth temperatures (around 500 °C), the elastic energy is the most important quantity that describes island formation and evolution [5–8]. Growth at higher temperatures (around 600 °C) causes intermixing between the substrate atoms and the growing film, producing islands with nonuniform composition [9,10]. The different mechanisms that lead to a particular composition profile were isolated in a controlled diffusion experiment [11].

The effects of alloy formation in the energy balance must be considered when formulating a realistic model for the island growth process [12–17]. Recently, a simulation of island evolution including intermixing was performed assuming only surface diffusion effects [14]. In contrast, the shape dependent equilibrium composition profile has been computed for alloy islands [17]. The thermodynamic potentials, which depend upon the system constraints, can provide a better understanding of the island size, shape, and composition profile evolution towards the equilibrium.

Here, the island composition profiles were experimentally evaluated upon different thermodynamic constraints. The flow of species between the system (islands) and a reservoir [wetting layer (WL)] was controlled by surface kinetics [11], permitting the investigation of two different situations: (a) an *open* system, where both Ge and Si could be exchanged with the WL, and (b) a *closed* system, in which Si exchange between the islands and the WL was inhibited.

The samples were grown by chemical vapor deposition (CVD), which allows the control of surface diffusion kinetics by annealing in different gas-phase environments after material deposition [18]. A reference sample (R) was grown under conditions favoring a graded composition profile along the radial and growth directions due to kinetic surface segregation [19]. This was accomplished by depositing 12 eq-ML [20]of Ge over 240 s at 600 °C onto a Si(001) substrate. These conditions were found to produce uniform ensembles ($\sim 9 \times 10^{9}$ cm^{-2}) of dome-shaped islands with 14.3 ± 2.3 nm height. The open and closed systems were implemented by growing two samples with the same experimental conditions as the R sample, but subsequently annealed for 10 minutes at the growth temperature in different environments. Sample O was treated in H_2 (10 Torr), with Ge and Si adatom surface diffusion taking place (open system). Sample C was annealed in a PH_3-H_2 atmosphere (1.4×10^{-5} Torr), which strongly inhibited Si surface diffusion, due to the P-Si bond formed with the Si atoms from the WL's surface [18]. As a result, only the Ge species could diffuse over the surface (closed system) [11]. Samples O and C exhibited islands with an average volume of approximately 35×10^3 and 38×10^3 nm^3, compared to 19×10^3 nm^3 for the reference sample. The overall dome shape of the islands were preserved upon annealing. Analysis of Grazing Incidence X-Ray Diffraction (GIXRD) data obtained at the Brazilian Synchrotron Light Source Laboratory yielded the Ge content and lattice spacing distribution within the islands [4,9,21], which allowed us to calculate all thermodynamic quantities.

Figure 1(a) shows the average composition profile for each island ensemble, assuming cylindrical symmetry. Sample R exhibits a high concentration gradient, reaching 1.0 Ge fraction at the island shell, and less than 0.50 fraction below 6 nm from the substrate surface. The Ge iso-composition contour at 0.50 is indicated by the solid black line for all samples. The annealed samples exhibit the following characteristics: (a) they portray a higher degree of intermixing when compared to R; (b) the 0.50 iso-composition lines for O and C occur at higher and lower heights, respectively, (c) both samples no longer display a pure Ge rich shell.

From the volume increase in the annealed samples, and using the average volume and concentration of R as a reference, the amount of Si uptake was estimated in $14 \pm 3 \times 10^3$ and $6 \pm 3 \times 10^3$ nm^3, and for Ge, in $3 \pm 3 \times 10^3$ and $14 \pm 3 \times 10^3$ nm^3 for samples O and C. Therefore, Si incorporation into the islands was reduced by a factor of ~3 for sample C, compared to sample O. This is likely coming from the WL subsurface and, to a lesser degree, the substrate. Nevertheless, the Ge average content for sample C remained constant upon annealing (0.75 ± 0.04 for sample R and 0.69 ± 0.03 for sample C), despite volume increase. For sample O, the average Ge concentration decreased significantly to 0.45 ± 0.02 because of Si surface diffusion [10,14].

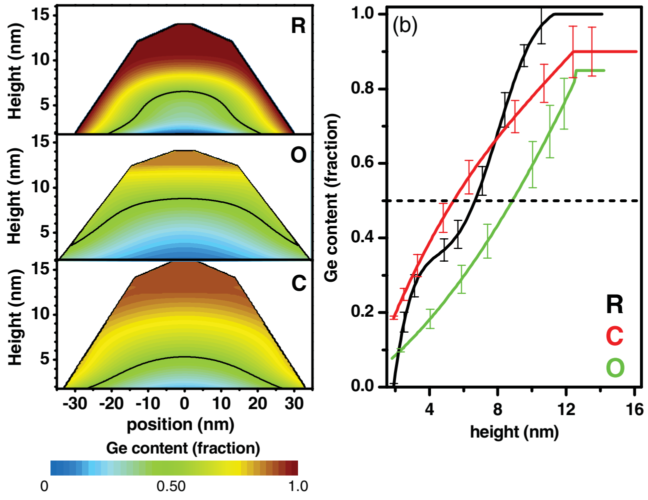

FIG. 1 (color). (a) Ge concentration (fraction) for samples R (reference), O (open), and C (closed). The black solid lines correspond to 0.50 Ge content. (b) Line scans taken along the growth direction at the island center for all samples for the Ge content as a function of the islands' height.

Figure 1(b) shows the Ge content line profile as a function of the height within the islands taken at the island center for each sample. As expected, the islands for the open system (sample O) are richer in Si, compared to samples R and C, due to the Si incorporation during annealing. The dome islands in sample C (closed system) show a higher Ge content up to 8 nm, when compared to sample R, demonstrating significant atom rearrangement within the domes during annealing.

The evolution of the composition profile depends on the generalized forces that govern the intermixing processes. For bulk epitaxial systems, there are two forces: mechanical forces due to the lattice mismatch (stress σ) and the chemical forces [22], represented by the chemical potential gradient $\nabla\mu$. These can be defined by $\sigma = \varepsilon_{\parallel}(C_{11}^2 + C_{11}C_{12} - 2C_{12}^2)/C_{11}$ and $\nabla\mu = (\hat{\rho}\frac{\partial}{\partial\rho} + \hat{z}\frac{\partial}{\partial z})[kT\ln(c)]$, where $\varepsilon_{\parallel}$ is the in-plane strain as measured by GIXRD, C_{11} and C_{12} are the composition dependent elastic constants of the Si-Ge alloy [1,23], $\hat{\rho}$ and $\hat{z}$ are the unit vectors for the radial and growth directions, k is the Boltzmann constant, T is the growth and annealing temperatures, and c is the Ge concentration. This bulklike analysis is justified for the systems investigated in this work because of the relatively large size of the islands (10^7 atoms) which allows the use of the bulk elastic constants, and the small ratio of surface to volume atoms of 2.5×10^{-3}, which minimizes the surface and interface effects. For example, the contribution of surface and interface stresses is estimated to be less than 20% of the average island stress [24].

The elastic maps [Fig. 2(a)] demonstrate that prior to annealing, a significant amount of stress exists at the perimeter of the island in sample R, which subsides for both annealed samples but most importantly for sample O. Looking at the island core and base, the reference sample exhibits a negligible stress. Upon annealing, while the stress is decreased further for the open system (sample O), and even changing sign within the island, the closed system (sample C) displays an increase in the internal stress. This can be understood by inspecting the gradient of the chemical potential [Fig. 2(b)]. For sample R, both the island core and base exhibit a higher chemical potential gradient than samples O and C. The chemical forces drive interdiffusion, despite the increase in the elastic energy for sample C. However, the top of the islands for all samples

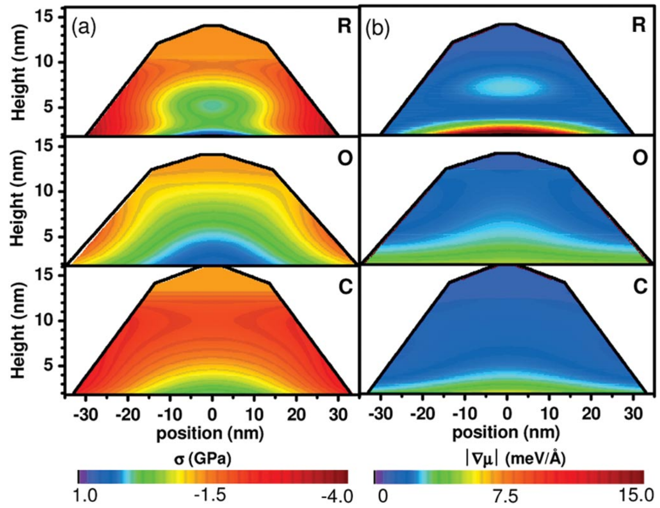

FIG. 2 (color). (a) Stress σ (GPa), with positive (negative) values for tensile (compressed) material, and (b) chemical potential gradient $|\nabla\mu|$ (meV/Å) maps for R (reference), O (open), and C (closed) samples (systems).

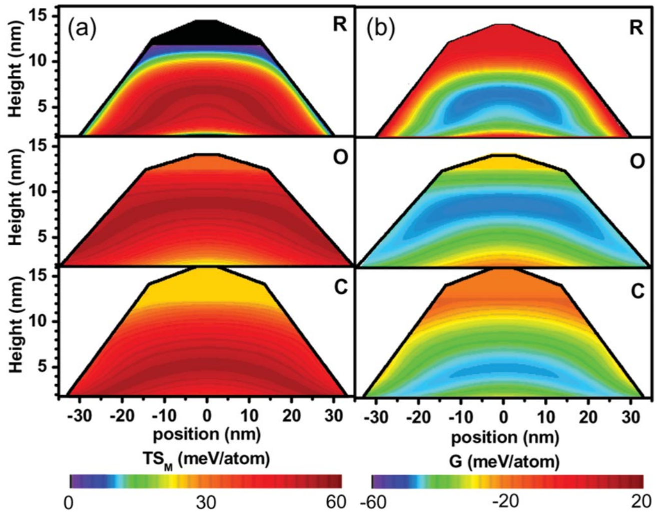

FIG. 3 (color). (a) Mixing entropy contribution TS_M (meV/atom) and (b) Gibbs free energy G (meV/atom) maps evaluated for samples R (reference), O (open), and C (closed).

shows a very small gradient, since the composition is constant (1.0, 0.90 and 0.85 in Ge fraction for samples R, C, and O, respectively). In this region, the stress is nevertheless finite (-1.3 GPa), which can cause intermixing. R exhibits a large variation of stress inside the island, which drives the compositional changes for the annealed samples. As a result, C and O show a more uniform distribution of stress, with C becoming more stressed. In conclusion, depending upon the constraints imposed on the system, chemical and mechanical forces have a distinct, yet direct impact on atom redistribution.

The complete picture of the evolution towards equilibrium requires the assessment of the Gibbs Free Energy (GFE). The description given by this thermodynamic potential encompasses the enthalpy of formation H and the mixing entropy S_M, both composition dependent. For the experiment described in this Letter, the GFE can be calculated as $G = H - TS_M$, with $H = E_{\mathrm{chem}} + E_{\mathrm{el}} + E_{\mathrm{surf}} + E_{\mathrm{lin}}$. The most important contributions to the enthalpic term are the chemical energy or mixing enthalpy $E_{\mathrm{chem}} = \Omega c(1 - c)$, and the lattice mismatch associated elastic energy $E_{\mathrm{el}} = 2\gamma\varepsilon_{\parallel}^2(1 + \nu)/(1 - \nu)$, where Ω is the interaction parameter, γ is the Young modulus, and ν is the Poisson ratio [1,23]. The other two energy terms, proportional to the surface area (E_{surf}) and the linear dimensions (E_{lin}) of the island will not be considered in our analysis because of the relatively large island size [25]. The entropic contribution related to the mixture formation can be approximated by $TS_M \cong -kT[c\ln(c) + (1 - c)\ln(1 - c)]$ [26–29]. For any Si-Ge alloy epitaxially grown on Si, at typical growth temperatures ($T \sim 873$ K), the entropic contribution dominates for $c < 0.9$.

Figure 3(a) shows the mixing entropy maps for all samples. For the open and closed systems, TS_M increases dramatically, specially at the island top. For both situations, the G is always negative, in contrast to the reference sample R [Fig. 3(b)], which displays positive values at the island shell. This result underscores the fact that as grown islands are not in local equilibrium state even when in low supersaturation (corresponding to a low deposition rate). For the closed system (C), the increase in TS_M compensates the increase in the elastic energy at the island core, as shown by the overall decrease in G. G is even lower for the open system (sample O), as a direct consequence of the decrease in the enthalpic term (due to enhanced intermixing with Si during annealing) and the increase in TS_M.

Table I shows the volume averaged values for the maps evaluated in this work. The stress mean value $\langle\sigma\rangle$ did not change significantly from R to C, although a local increase in σ was found at the island core for C. In contrast, the open system shows a robust decrease in $\langle\sigma\rangle$ due to alloying of the islands with the Si reservoir. Comparing the volume averaged gradient of chemical potential $\langle|\nabla\mu|\rangle$ for all samples, the smallest $\langle|\nabla\mu|\rangle$ was found for sample C,

TABLE I. Volume averaged values for the maps obtained for the different samples. For the gradient of the chemical potential, the uncertainties represent the standard deviation of the values within the islands displayed in Fig. 2. The last line corresponds to the Gibbs free energy calculated for a two dimensional film with the same average Ge content as the measured samples.

	Sample		
	R	C	O
$\langle c\rangle$ (fraction)	0.75 ± 0.04	0.69 ± 0.03	0.45 ± 0.02
$\langle\sigma\rangle$ (GPa)	1.6 ± 0.2	1.8 ± 0.2	0.8 ± 0.1
$\langle\|\nabla\mu\|\rangle$ (meV/Å)	1.9 ± 0.9	0.9 ± 0.2	1.5 ± 0.5
$\langle TS_M\rangle$ (meV/atom)	33 ± 3	44 ± 3	48 ± 2
$\langle G\rangle$ (meV/atom)	-26 ± 5	-36 ± 5	-43 ± 3
G_{film} (meV/atom)	-22	-29	-41

which validates the assumption of a closed system. Sample O exhibits a smaller $\langle|\nabla\mu|\rangle$ when compared to R, due to the evolution of the open system towards equilibrium. Both open and closed systems show an increase in $\langle TS_M\rangle$. As a result, both annealed samples have lower $\langle G\rangle$, compared to R. In particular, $\langle G\rangle$ is the lowest for O, as it is more likely for an open system to achieve a minimum energy configuration.

The GFE calculated for a two dimensional film G_{film} with the same Ge average content as the measured samples represent an upper limit, as they do not include the additional relaxation in the Si substrate. Therefore, the measured values of $\langle G\rangle$ should indicate how efficiently the energy minimization takes place upon island formation and evolution. For samples R and O, $\langle G\rangle$ is very close to G_{film}, corresponding to a kinetically stable configuration. For the closed system, a more pronounced relaxation occurs. This observation has a very important consequence for the final island size, shape, and composition profile. Upon comparing samples O and C, volumes differing by less than 10% were found, yet the composition is $\sim$1.5 times higher for the bigger islands (sample C). Noting that the island volume should scale with ε^{-6} ($\propto c^{-6}$) for islands of uniform composition [8], the expected volume increase would have been 20 fold. This unexpected result demonstrates the determining factor of composition profile on island size during growth and annealing [30].

In conclusion, closed and open systems were implemented by controlling surface diffusion kinetics. Furthermore, the composition profile evolution of the Si-Ge islands towards equilibrium were followed. The evaluation of the thermodynamic potentials in both systems allowed for additional evidence of the importance of entropy for alloying. For the open system, an overall decrease in the GFE was found due to the Si surface diffusion process, leading to a decrease in the Ge content. For the closed system, by minimizing the chemical potential gradient, a decrease in the GFE was observed, despite the unexpected increase in the elastic energy. Finally, atom rearrangement within the islands producing particular composition profiles can have a determining factor for the island size. This result could be mapped to other material systems, if an appropriate kinetic control can be envisaged.

The authors M. S. L. and G. M. R. thank FAPESP Contract No. 03/09374-9, CNPq, and HP Brazil for financial support.

---

*Corresponding author: gmedeiros@lnls.br

[1] J. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic Press, New York, 1993).

[2] L. Ratke and P. W. Voorhees, *Growth and Coarsening: Ostwald Ripening in Material Processing* (Springer, New York, 2002).

[3] G. Costantini *et al.*, Appl. Phys. Lett. **85**, 5673 (2004).

[4] R. Magalhaes-Paniago *et al.*, Phys. Rev. B **66**, 245312 (2002).

[5] V. A. Shchukin *et al.*, Phys. Rev. Lett. **75**, 2968 (1995).

[6] G. Medeiros-Ribeiro *et al.*, Science **279**, 353 (1998).

[7] F. M. Ross *et al.*, Phys. Rev. Lett. **80**, 984 (1998).

[8] A. Rastelli *et al.*, Phys. Rev. Lett. **87**, 256101 (2001).

[9] A. Malachias *et al.*, Phys. Rev. Lett. **91**, 176101 (2003).

[10] G. Katsaros *et al.*, Phys. Rev. B **72**, 195320 (2005).

[11] M. S. Leite *et al.*, Phys. Rev. Lett. **98**, 165901 (2007).

[12] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).

[13] G. Medeiros-Ribeiro and R. Stanley Williams, Nano Lett. **7**, 223 (2007).

[14] Yuhai Tu and J. Tersoff, Phys. Rev. Lett. **98**, 096103 (2007).

[15] C. Lang *et al.*, Phys. Rev. B **72**, 155328 (2005).

[16] G. Hadjisavvas *et al.*, Phys. Rev. B **72**, 075334 (2005).

[17] N. V. Medhekar, V. Hegadekatte, and V. B. Shenoy, Phys. Rev. Lett. (to be published).

[18] T. I. Kamins, G. Medeiros-Ribeiro, D. A. A. Ohlberg, and R. Stanley Williams, J. Appl. Phys. **94**, 4215 (2003).

[19] J. Tersoff, Appl. Phys. Lett. **83**, 353 (2003).

[20] 1 eq-ML Ge = 6.33×10^{14} Ge atoms/cm^2

[21] An adventitious native oxide layer does not pose significant problems for the data analysis and interpretation of the composition profiles, specially for the dome-shaped islands investigated in this Letter, which have a small surface area to volume ratio [4].

[22] Strictly speaking, in a thermodynamic sense, the chemical forces are generalized forces, which are defined by the gradient of the relevant potential.

[23] The parameters used here were: $C_{11} = 16.57 \times 10^{10}$ N/m^2 and $C_{12} = 6.39 \times 10^{10}$ N/m^2 for Si, and $C_{11} = 12.89 \times 10^{10}$ N/m^2 and $C_{12} = 4.83 \times 10^{10}$ N/m^2 for Ge, $\Omega = 4.06$ meV/atom, $\gamma^{\mathrm{Si}} = 5.09 \times 10^{10}$ N/m^2, $\gamma^{\mathrm{Ge}} = 4.09 \times 10^{10}$ N/m^2, $\nu^{\mathrm{Si}} = 0.278$, and $\nu^{\mathrm{Ge}} = 0.273$ [1].

[24] P. Müller and O. Thomas, Surf. Sci. **465**, L764 (2000).

[25] P. Raiteri and Leo Miglio, Phys. Rev. B **66**, 235408 (2002).

[26] Charles Kittel and Herbert Kroemer, *Thermal Physics* (W. H. Freeman, San Francisco, 1980), 2nd ed.

[27] J. E. Bernard and Alex Zunger, Phys. Rev. B **44**, 1663 (1991).

[28] A. Malachias *et al.*, Phys. Rev. B **72**, 165315 (2005).

[29] Although ordering has been predicted to be nonfavored thermodynamically [27], there is experimental evidence for ordering in Si-Ge islands grown by Molecular Beam Epitaxy [28]. Here, the effects of ordering on the entropy were neglected, as similarly grown islands (sample A in reference [28]) exhibit an ordering parameter of $s = 0.15$ (with $s = 0$ corresponding to a perfectly random alloy, and $s = 1$ to a perfectly ordered alloy).

[30] Conventional x-ray diffraction patterns exhibited a narrower (broader) linewidth for sample C (O) when compared to sample R (not shown). This is an additional evidence for efficient atom redistribution.