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Thermodynamics of Coherently-Strained Ge_xSi_{1-x} Nanocrystals on Si(001): Alloy Composition and Island Formation

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ABSTRACT

We determined the enthalpic and entropic contributions to the thermodynamics of coherently strained nanocrystals grown via deposition of pure Ge on Si(001) surfaces at 600 and 700 °C by analyzing their composition profile and local strain. We found that the free energy associated with the entropy of mixing, which drives Ge_xSi_{1-x} alloy formation, was significantly larger than the relaxation enthalpy that produces the islands. Thus, entropy plays a significant role in the evolution of the size and shape of the islands during growth through the strong thermodynamic drive to form an alloy.

For many lattice-mismatched systems, a small amount of one material deposited onto a single-crystal surface of another will yield coherently strained heteroepitaxial nanocrystals that can have atomic-like electronic properties. Over the past several years, many theoretical and experimental investigations have interpreted this nanocrystal formation and evolution as either a thermodynamic or kinetic process.[1−7] In most cases, the driving force for island formation and shape change is considered to be the relaxation of the elastic energy that arises from the lattice mismatch between the nanocrystals and the substrate. The stability of an island ensemble has been discussed in the context of elastic, surface, and line energy components. In the thermodynamic scenario, a preferred island size exists that is metastable with respect to Ostwald ripening;[1] subsequent forced growth by continued deposition results in a shape change[2−6] that can be reversed by annealing to induce alloy formation in the islands.[7] In the kinetic scenario, observed increases in the average island size over time are ascribed to Ostwald ripening,[8] and shape changes occur because of discontinuities of the island chemical potential, producing an anomalous coarsening process,[3] or because of island−island interactions.[2,6] In most studies, the islands were implicitly assumed to have a constant and uniform composition over time. The role of the island composition was believed to be secondary; the average size of an island ensemble was determined by the strain, which in turn depended on the island chemical composition through Vegard's law (the island radius displays a dependence on the strain ϵ as $R \propto 1/\epsilon^2$).[9] However, if the composition and thus the strain are time-dependent, they will

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have a major impact on the evolution of the island size distribution.

More recently, several groups have discovered that the island composition was not only different from the nominally deposited material, but it was also nonuniform.[8,10−12] The observed composition profiles have been associated with different mechanisms that produce particular composition configurations, which may provide a clue to the island formation mechanism.[12−14] If the formation mechanism can be controlled, it may be possible to tailor the composition profile and thus the electronic confining potential. Here we show that the free energy that determines the nanocrystal size, shape, and composition includes mechanical energy and entropy terms, with the latter being significantly larger for typical island growth temperatures.

The system analyzed here is Ge on Si (001), which displays the full range of behavior for coherently strained nanocrystal islands. Two samples were grown under two very different conditions: sample C was grown at 600 °C by CVD at a rate of 3 ML/min. Sample M was grown at 700 °C by MBE at a rate of 1 ML/min. For both samples, the total amount of deposited material was 12 equiv ML of Ge (1 eqML of Ge $= 6.3 \times 10^{14}$ atoms/cm^2). Atomic force microscope (AFM) and anomalous X-ray diffraction (AXRD) experiments were performed[15] to obtain 3D structural and chemical maps of the highly monodisperse islands. The average island radii were 32 ± 4 and 51 ± 4 nm with heights of 14 ± 2 nm and 19 ± 2 nm for samples C and M, respectively.

Figure 1 shows the composition profile for samples C and M grown at different temperatures as well as the corresponding composition histogram as determined from AXRD.[15] The average Ge mole fraction x for samples C and M determined from the AXRD data are 77 ± 5% and 70 ± 5%, respectively. Examination of the size and composition data yields the following observations: (1) the island surface and top are Ge rich for both samples, (2) there is a significant amount of Si within the island base, (3) the dome M to C radius ratio (∼1.6) is larger than that predicted from the simple $1/\epsilon^2$ dependence that results from their average compositions (∼1.2), and (4) the composition inside the domes is not uniform, in contrast to the predictions for an equilibrated dome by several Monte Carlo simulation studies.[16−18]

To understand the observed composition profiles, both the thermodynamics of mixing[19] and mechanical energies[15] should be evaluated. The Gibbs free energy is $G = H - TS$, where H is the enthalpy, T is the growth temperature, and S is the entropy. The enthalpy of formation H has two components: $H = E_{\text{elastic}} + E_{\text{chemical}}$. The elastic component E_{elastic} includes island bulk, surface, and edge strain as well as island−island interactions,[1,4] which at the atomic scale modify the bond angles and lengths. Table 1 lists the elastic energy stored in 2D films on unrelaxed substrates calculated by elasticity theory as well as the average experimental values evaluated for samples C and M.[15] As a reference, for an unstrained $Si_{0.5}Ge_{0.5}$ random alloy 2D film, E_{elastic} is ∼2.4 meV/atom, which arises from the bond angle and length variations.[20] For the case of a 2D $Si_{0.5}Ge_{0.5}$ layer coherently strained onto unrelaxed Si, E_{elastic} is ∼8 meV/atom.[20] An

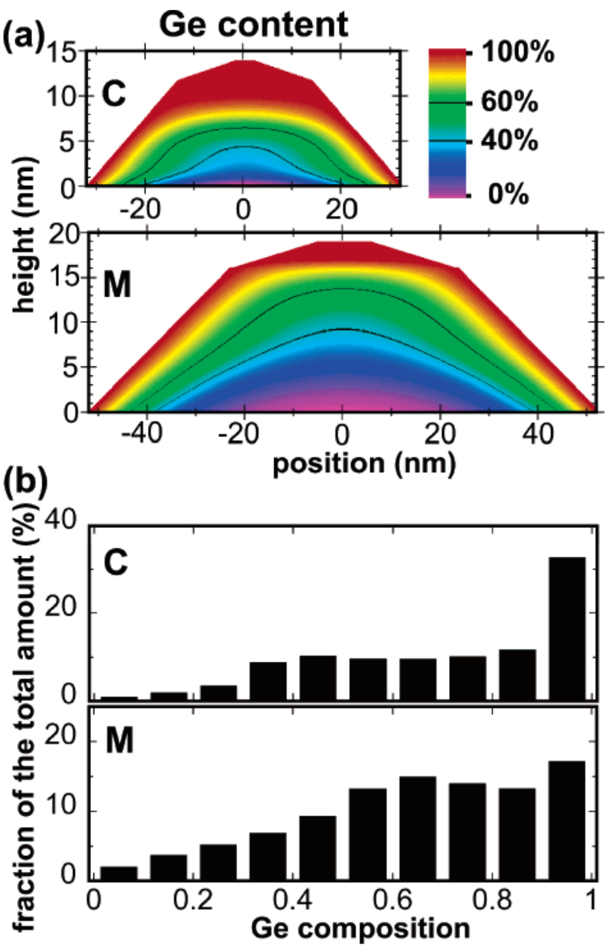

Figure 1. (a) Composition profiles as obtained from AXRD data.[15] The black lines correspond to isoconcentration contours at 40% and 60% Ge content. (b) Composition histogram inferred from the composition maps (a) for both samples. The bin that corresponds to nearly pure Ge is primarily surface material.

Table 1. Average Energies for Islands Grown under Different Conditions (meV/atom)

average free energy contributions	600 °C, $x = 0.77$ (meV/atom)	700 °C, $x = 0.70$ (meV/atom)
enthalpy of mixing (E_{chemical})[a]	2.4 ± 0.1	2.8 ± 0.1
entropy of mixing ($-TS_{\text{mix}}$)[b]	−35 ± 7	−44 ± 6
free energy of mixing (G_{mix})	−33 ± **7**	−41 ± **6**
elastic energy in dome[c]	8 ± 1	5.3 ± 0.5
elastic energy in substrate[d]	∼8	∼5
total elastic energy[e]	∼16	∼10
elastic energy of an alloy film[f]	22	20
relaxation energy of dome[g]	∼−6	∼−10

[a] Calculated from $E_{\text{chemical}}(x) = w \times x \times (1 - x)$, where $w = 4 \times E_{\text{chemical}}(0.5) \sim 4$ meV/atom. [b] Calculated from $-TS_{\text{mix}}(x) = kT(x \ln x + (1 - x) \ln(1 - x))$. [c] Determined from experimental AXRD data (ref 15) and elastic constants of alloys. [d] Estimated to be equal to the elastic energy stored in an island. [e] Estimated total strain energy in dome and substrate per atom in the dome. [f] Calculated from elasticity theory for an uniform layer constrained to a Si substrate with a composition derived from that of a film with the same mixing entropy of that of the average dome. [g] Estimated average relaxation energy for Domes compared to an uniform film of a composition that exhibits the same average entropy.

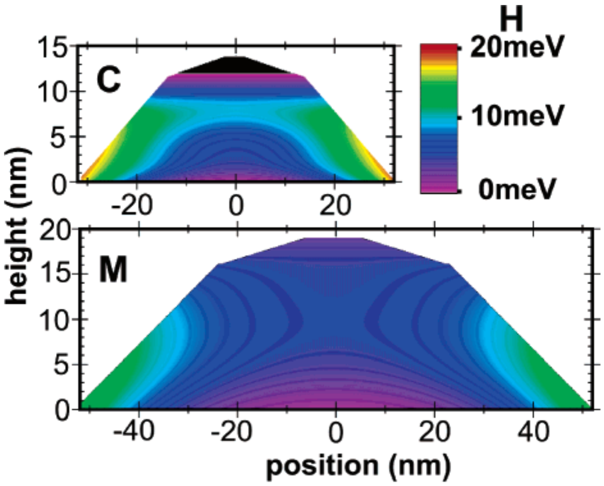

Figure 2. The enthalpies for domes C and M on a per atom basis. Regions of maximum strain are at the periphery of the islands near the substrate.

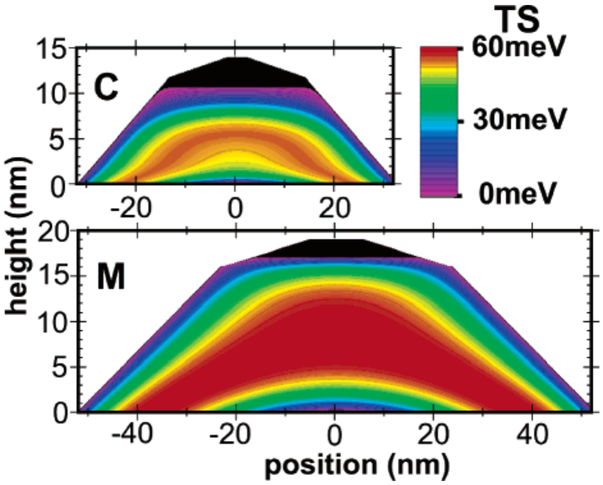

Figure 3. Entropy contribution to the Gibbs free energy per atom in the alloyed domes.

important issue to be considered is that, in real systems, the substrate is relaxed and thus also stores elastic energy.[21] These strain fields are tensile directly under an island and then become compressive in the region outside the outer edge of the island. By equipartition, the strain fields in the substrate should contain about the same amount of energy as the strain in the islands themselves. However, because the volume over which the strain extends is so large, the magnitude of the substrate strain is much smaller than in the islands, and moreover, it changes sign depending on the position in the substrate. Thus, it is very difficult to determine this strain and the energy associated with it experimentally. We will approximate the substrate strain energy by setting it equal to the measured island strain energy.

The enthalpy of mixing E_{chemical} comes from charge transfer between the atomic species, and this contribution can be evaluated by first-principles total-energy pseudopotential calculations for SiGe alloys.[20−23] Such a treatment is well approximated by the regular solution model

$$E_{\mathrm{chemical}}(x) = w \times x \times (1 - \mathrm{x}) \tag{1}$$

where the interaction parameter $w = 4 \times E_{\mathrm{chemical}}(0.5) \approx 4$ meV/atom and x is the mole fraction of Ge in the alloy.[20,22−24] Because $w > 0$, bulk Ge and Si should phase-separate in bulk alloys at equilibrium below a critical temperature of about 170 K.[22] Interestingly, ordering in islands has been reported for samples grown at temperatures as high as 840 °C,[25] despite reports showing that, at temperatures above 700 °C, no ordering could persist in 2D films.[26] The issue of ordering is important because it lowers the entropy compared to a random alloy, and depending on the order parameter, which was not measured for the samples reported here, could have a 10−20% effect. This is not large enough to effect our conclusions in this paper.

The total enthalpy contours where the strain contribution was taken from the experimental measurement and the chemical contribution from the calculations based on the compositions of samples C and M are displayed in Figure 2. The main observation to be made is that, for both systems, the perimeter of the island stores the largest amount of enthalpy, which is dominated by the elastic component. The average values for each component, $E_{\mathrm{chem}}(x)$ and $E_{\mathrm{elastic}}(x)$, are represented in Table 1.

The entropic contribution to the Gibbs free energy of random alloys is given by[19]

$$TS_{\mathrm{mix}}(x) = -kT(x \ln x + (1 - x) \ln(1 - x)) \tag{2}$$

where we assume the activities for Ge and Si are well approximated by the mole fractions x and $1 - x$, respectively, because E_{chemical} is small. Figure 3 shows the spatial contours of the mixing entropy TS_{mix} for samples C and M. The regions in the islands that are nearly pure Ge or Si have $TS_{\mathrm{mix}} \approx 0$, and the region with x near 0.5 has the largest TS_{mix}.

Summarized in Table 1 are the average thermodynamic quantities determined from Figures 2 and 3, along with calculations for uniform films of Ge alloys. Comparing these values allows us to understand the magnitude of the thermodynamic drivers for both alloy and island formation.

The free energy of mixing for Ge and Si contains a large negative entropy contribution and a much smaller positive enthalpy contribution and is independent of the geometry of the alloy. We chose uniform alloy 2D films as a reference for our comparisons. The composition for those films was chosen to produce the same mixing entropy as samples C and M. That allows us to determine the difference in enthalpy between a 2D film and a dome population, e.g., ΔH_{dome}. This is the elastic energy stored in the domes and the substrate (which we approximate with twice the experimentally measured elastic energy in the dome population) minus the elastic energy in the film (which was calculated for an unrelaxed substrate, so all of the energy is stored in the film). The values of ΔH_{dome}, which are averages, are −6 and −10 meV/ atom for dome populations C and M, respectively. These values are negative, as they must be, because the domes are more stable than uniform films, and they depend strongly on the mole fraction of Ge. There is also a configurational entropy associated with the population of domes, but it is negligible compared to the enthalpy.

For both populations, the free energy of mixing is about 4−5 times larger in magnitude than ΔH_{dome}. The lower enthalpy of the dome population with respect to a uniform film determines the morphology of the alloy on the Si substrate. However, the fact that the free energy of mixing is so much larger means that the thermodynamic drive to form an alloy is much stronger. Because the size of a dome is primarily determined by its composition, this means that mixing entropy plays a major role in the evolution of island sizes and thus also shape transitions in heteroepitaxial island-forming systems. This issue has not been explicitly recognized until now.

In summary, we evaluated the enthalpy of formation and the free energy of mixing for two populations of epitaxial Ge_xSi_{1-x} alloy domes on a Si(001) substrate. We found that the mixing entropy term in the free energy (averaged over the dome population) is several times larger in magnitude than the dome enthalpy of formation. Thus, the chemical drive to form an alloy is much stronger than that to form the population of domes, and this should be explicitly considered in the evolution of island populations during growth and annealing.

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References

(1) Shchukin, V. A.; Ledentsov, N. N.; Kop'ev, P. S.; Bimberg, D. *Phys. Rev. Lett.* **1995**, *75*, 2968. Meixner, M.; Schöll, E.; Shchukin, V. A.; Bimberg, D. *Phys. Rev. Lett.* **2001**, *87*, 236101.
(2) Floro, J. A.; Lucadamo, G. A.; Chason, E.; Freund, L. B.; Sinclair, M.; Twesten, R. D.; Hwang, R. Q. *Phys. Rev. Lett.* **1998**, *80*, 4717.
(3) Ross, F. M.; Tersoff, J.; Tromp, R. M. *Phys. Rev. Lett.* **1998**, *80*, 984. Ross, F. M.; Tromp, R. M.; Reuter, M. C. *Science* **1999**, *286*, 1931.
(4) Medeiros-Ribeiro, G.; Bratkovski, A. M.; Kamins, T. I.; Ohlberg, D. A. A.; Williams, R. S. *Science* **1998**, *279*, 353. Robert, E.; Rudd, G. A. D.; Briggs, A. P.; Sutton, G.; Medeiros-Ribeiro; Williams, R. S. *Phys. Rev. Lett.* **2003**, *90*, 146101.
(5) Vine, D. J.; Jesson, D. E.; Morgan, M. J.; Shchukin, V. A.; Bimberg, D. *Phys. Rev. B* **2005**, *72*, 241304.
(6) Floro, J. A.; Sinclair, M. B.; Chason, E.; Freund, L. B.; Twesten, R. D.; Hwang, R. Q.; Lucadamo, G. A. *Phys. Rev. Lett.* **2000**, *84*, 701.
(7) Kamins, T. I.; Medeiros-Ribeiro, G.; Ohlberg, D. A. A.; Williams, R. S. *Appl. Phys. A* **1998**, *67*, 727.
(8) Zinke-Allmang, M.; Feldman, L. C.; Grabow, M. H. *Surf. Sci. Rep.* **1992**, *16*, 377.
(9) Rastelli, A.; Kummer, M.; von Känel, H. *Phys. Rev. Lett.* **2001**, *87*, 256101.
(10) Malachias, A.; Kycia, S.; Medeiros-Ribeiro, G.; Magalhães-Paniago, R.; Kamins, T. I.; Williams, R. S. *Phys. Rev. Lett.* **2003**, *91*, 176101.
(11) Floyd, M.; Zhang, Y.; Driver, K. P.; Drucker, J.; Crozier, P. A.; Smith, D. J. *Appl. Phys. Lett.* **2003**, *82*, 1473.
(12) Denker, U.; Stoffel, M.; Schmidt, O. G. *Phys. Rev. Lett.* **2003**, *90*, 196102.
(13) Katsaros, G.; Costantini, G.; Stoffel, M.; Esteban, R.; Bittner, A. M.; Rastelli, A.; Denker, U.; Schmidt, O. G.; Kern, K. *Phys. Rev. B* **2005**, *72*, 195320.
(14) Leite, M. S.; Medeiros-Ribeiro, G.; Kamins, T. I.; Williams, R. S. submitted.
(15) Medeiros-Ribeiro, G.; Malachias A.; Kycia, A, S.; Magalhaes-Paniago, R.; Kamins, T. I.; Williams, R. S. *Appl. Phys. A* **2005**, *80*, 1211.
(16) Sonnet, P.; Kelires, P. C. *Phys. Rev. B* **2002**, *66*, 205307.
(17) Hadjisavvas, G.; Kelires, P. C. *Phys. Rev. B* **2005**, *72*, 075334.
(18) Lang, C.; Cockayne, D. J. H.; Nguyen-Manh, D. *Phys. Rev. B* **2005**, *72*, 155328.
(19) Lewis, G. N.; Randall, M. *Thermodynamics*; revised by Pitzer, K. S., Brewer, L., Eds.; McGraw-Hill: New York, 1961; pp 281−284.
(20) Bernard, J. E.; Zunger, A. *Phys. Rev. B* **1991**, *44*, 1663.
(21) Raiteri, P.; Miglio, L.; Valentinotti, F.; Celino, M. *Appl. Phys. Lett.* **2002**, *80*, 3736.
(22) Kelires, P. C.; Tersoff, J. *Phys. Rev. Lett.* **1989**, *63*, 1164.
(23) Koiller, B.; Robbins, M. O. *Phys. Rev. B* **1989**, *40*, 12554.
(24) Venezuela, P.; Dalpian, G. M.; Antônio, J.; da Silva, Fazzio, A. *Phys. Rev. B* **2001**, *64*, 193202.
(25) Malachias, A.; Schülli, T. U.; Medeiros-Ribeiro, G.; Cançado, L. G.; Stoffel, M.; Schmidt, O. G.; Metzger, T. H.; Magalhães-Paniago, R. *Phys. Rev. B* **2005**, *72*, 165315.
(26) See, for example: Whiteaker, K. L.; Robinson, I. K.; Van Nostrand, J. E.; Cahill, D. G. *Phys. Rev. B* **1998**, *57*, 12410 and references therein.

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