The equilibrium composition in Ge_xSi_{1-x}/Si self-assembled alloy quantum dot*

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(Received 13 November 2009; revised manuscript received 9 March 2010)

The equilibrium composition in strained quantum dot is the result of both elastic relaxation and chemical mixing effects, which have a direct relationship to the optical and electronic properties of the quantum-dot-based device. Using the method of moving asymptotes and finite element tools, an efficient technique has been developed to compute the composition profile by minimising the Gibbs free energy in self-assembled alloy quantum dot. In this paper, the composition of dome-shaped Ge_xSi_{1-x}/Si quantum dot is optimized, and the contribution of the different energy to equilibrium composition is discussed. The effect of composition on the critical size for shape transition of pyramid-shaped GeSi quantum dot is also studied.

Keywords: equilibrium composition, quantum dot, method of moving asymptotes

PACC: 6865, 4620, 8116D

1. Introduction

Self-assembled GeSi quantum dot (QD) has received special attention not only because it is successfully applied in photonic application, but also it plays an important role in the semiconductor industry.[1−5] The equilibrium composition has a direct relationship to the optical and electronic properties of the self-assemble alloy QD. Since the composition is coupled with the shape, strain, and growth environment, obtaining the composition profiles is still a tough work. Several experimental papers have reported the composition profiles of Ge/Si in heteroepitaxial Ge QD grown on Si(001) substrates by chemical vapour deposition (CVD) or molecular beam epitaxy (MBE).[6−8] Several groups contrived to establish theoretical computation for equilibrium composition in recent years.[9−11] But the theoretical studies have limitations to gain the exact equilibrium composition profiles, such as the convergence of theoretical computation is extremely slow. So this field is still of much concern to many researchers.

The key factor that influences the composition distribution is the competition among different energy contributions, such as elastic energy and chemical mixing energy. Meanwhile, the entropy contribution must be taken into account at high temperatures. While the QD is formatting, the system attempts to release the strain, stored in both QD and substrate. This process, which provides a channel to reduce the lattice mismatch, will facilitate Si congregate at the compressed base and Ge at the relaxed top. On the other hand, the entropy forces the system towards uniform alloying. For a given shape, size, and average composition of a strained dot, the composition can be obtained by minimizing the Gibbs free energy which includes entropy, elastic energy and chemical mixing energy. Monte Carlo methods and quadratic programming methods have been employed for such problems,[11,12] but the speed of those two methods are not satisfactory.

Based on the method invented by Medhekar,[11] this paper introduces the effect of entropy and enthalpy on composition distribution of QD and develops a new faster method by combining the method of moving asymptotes (MMA) and finite element method (FEM). Medhekar also indicated that different energy

*Project supported by the National High Technology Research and Development Program of China (Grant No. 2009AA03Z405), the National Natural Science Foundation of China (Grant Nos. 60908028, 60971068, 10979065, and 10947150) and the High School Innovation and Introducing Talent Project of China (Grant No. B07005).

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influences the composition distribution in different situations. For example, at low growth temperatures, elastic energy plays the most important role in QD formation,[13−16] but when the temperature is higher (around 873 K), the entropy of mixing effect makes the largest contribution.[8] So the continuum elasticity theory is employed for rigorous treatment of elastic energy, and the Gibbs free energy is evaluated at the different temperatures in the process of optimizing the composition of dome-shaped Ge_xSi_{1-x}/Si QD. A fast and simple tool for discussing the equilibrium composition of QD with a given average composition and shape is obtained by the method in this paper, which can be used also to solve any other optimization problems.

2. Methodology

In the optimization problem, the process is to find the appropriate position of Si and Ge in QD, and minimize the total energy of the system. The selection of objective function has a direct relation to the optimization consequence. In order to gain the accurate composition profile in QD, Gibbs free energy (G) is considered to be the objective function which contains entropy (S) and enthalpy (H), and it can be calculated by $G = H - TS$; the entropic contribution to G can be approximated by

$$TS \approx -kT[cln(c) + (1-c)\ln(1-c)], \tag{1}$$

where c is the composition of QD,[17−19] T is temperature, and k is Boltzmann's constant. The enthalpy can be obtained by

$$H = E_{\text{chemical}} + E_{\text{elastic}} + E_{\text{surf}} + E_{\text{lin}}. \tag{2}$$

When the size of the QD is very large, the energy that is proportional to surface area (E_{surf}) and linear dimension (E_{lin}) of the QD is very small,[20] so the chemical energy and elastic energy are the two main contributions to H. The chemical energy can be written as

$$E_{\text{chemical}} = \Omega c(1-c), \tag{3}$$

where Ω is the chemical interaction parameter. The elastic energy is given by

$$E_{\text{elastic}} = \frac{1}{2}\int \sigma^t(\varepsilon - \varepsilon_0)\mathrm{d}V, \tag{4}$$

where the stress (σ) and strain (ε) components can be related by using a stiffness matrix D, and $\varepsilon_0 = \varepsilon_{\text{m}}c(x)$ is the composition-dependent mismatch strain in the QD, ε_{m} is the initial strain in the QD system. The initial strain is the lattice mismatch of the materials in a QD region, while it is zero in the surrounding barriers. The details about the calculations of the strain distribution can be found in our previous publications,[21−24] here we will use the results directly.

Like the other mathematical optimization methods, MMA[25] is a useful optimization tool, which has been used successfully in lots of topological optimization problems. This method introduces the convex function for approximating the primitive function which is based on one-step Taylor expansion approximation, and the implicit function (primitive function) can be approximated by a series of discrete and explicit function (convex function), and finally the optimization problem turns to solving the sequence of explicit subproblems. In other words, MMA simplifies the complex optimization problem by introducing the moving asymptotes. The key in the MMA optimization is to compute the sensitivities of the objective function to variables. The sensitivities are used to updating the variables which will be the initial values in the next iteration of the MMA process. In this condition, FEM is an excellent tool to achieve the sensitivities by adjoint methods, while the stress and strain problem can also be solved efficiently by FEM.

To perform the optimization we need combine MMA and FEM to compute sensitivities of the objective function to variables and find the optimal solution. The purpose of optimizing the composition distribution in a QD is to minimize the total free energy of the system. First, we build a three-dimensional QD FEM model, combining the stress-strain mode and sensitivity analysis mode in FEM. In stress-strain mode, we should introduce the initial strain $\varepsilon_0 = \varepsilon_{\text{m}}c(x)$ in a QD region ($\varepsilon_{\text{m}} = 0.04$ for GeSi/Si QD). In sensitivity analysis mode, the objective function is the total Gibbs free energy, the initial variable is the initial composition distribution and the constraint is the average composition. The solution for FEM is to obtain the value of objective function, and the sensitivities of the objective function to composition. Secondly, we should put the initial variables, the value of objective function and the sensitivities into the MMA algorithm for obtaining the new com-

position distribution of QD which has the smaller free energy. Next, we substitute the new composition in the FEM for obtaining the new value of objective and the sensitivities. Such iteration will go on until it satisfies the convergence condition, i.e., the change of the objective values between adjacent two iterations is less than 10^{-21} J (the value of objective is given in units of 10^{-15} J in this paper).

3. Applications

The dome-shaped Ge_xSi_{1-x}/Si QDs have been obtained by CVD or MBE under different conditions,[26,27] and the composition of the QD is studied by several groups. In order to interpret and guide the experiment more accurately, we study the composition of the dome-shaped QD with an average volume 3.8×10^4 nm^3 and a height 16 nm. The average composition of QD is 0.69, and about 1.2×10^6 atoms are involved in computation. The model of dome-shaped QD is given in Fig. 1. An extra fine mesh is used in the QD FEM model to obtain the accurate solution. Because both the QD and substrate have the strain release when QD grows, it is necessary to consider the contribution of it to elastic energy. A large substrate must be taken for improving the calculation accuracy. Periodic boundary condition is considered for substrate lateral face, while fixed boundary condition for substrate bottom, and free condition for the other surfaces. The anisotropic experimental material constants[28] and chemical interaction parameter[9] for pure Ge, Si and Ge_xSi_{1-x} alloy are shown in Table 1.

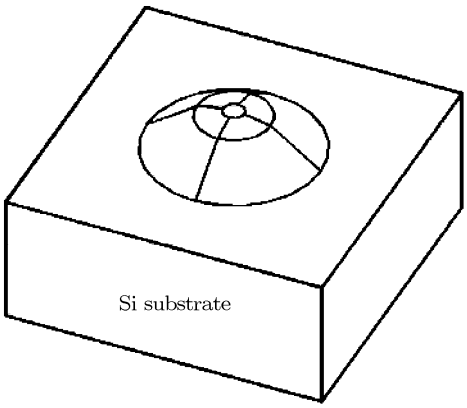


Fig. 1. The model of the dome-shaped QD.

Table 1. Material constants and chemical interaction parameter.

material	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa	lattice parameter/nm	chemical interaction parameter/10^8 J·m^{-3}
Ge	128.9	48.3	66.8	0.5431	
Si	165.7	63.9	79.6	0.5658	
Ge_xSi_{1-x}	165.7–37.3x	63.9–15.6x	79.6–12.8x	$5.431+0.2x+0.027x^2$	3.47

In order to study the contribution of entropy to equilibrium composition in strained QD, the equilibrium composition in dome-shaped QD is measured at 300, 600 and 900 °C. The final consequences at different temperatures are shown in Fig. 2(a). The Ge content along the vertical direction at the QD centre for all conditions is shown in Fig. 2(b). At high temperatures, the contribution to Gibbs free energy from entropy plays a major role and leads the system towards uniformity. The composition at the corner of the island is always inhomogeneous, because the strain is high at that place.[29] On the contrary, at low temperatures, the system becomes inhomogeneous because the elastic energy is dominant. The usual experimental temperature is about 600 °C, thus the distinctly inhomogeneous Ge profile is observed in the experiment.[27] Ignoring the effect of strain distortion at the corner of QD, we find that Ge content at the top of the island can reach 0.75 after optimization, which agrees with the profiles from the experiment.[27] The QD formation and evolution are the result of competition between thermodynamic and kinetic processes. In this paper we employ a simplified kinetic scheme in our model, while some atomic-scale information is missing (such as, Ge atoms are not allowed to diffuse to the Si background). In this aspect, our method has the same limitations as the above methods.[9–11] So our simulation still cannot completely agree with experimental results. While qualitative investigation in our work may give some useful directions for experiments.

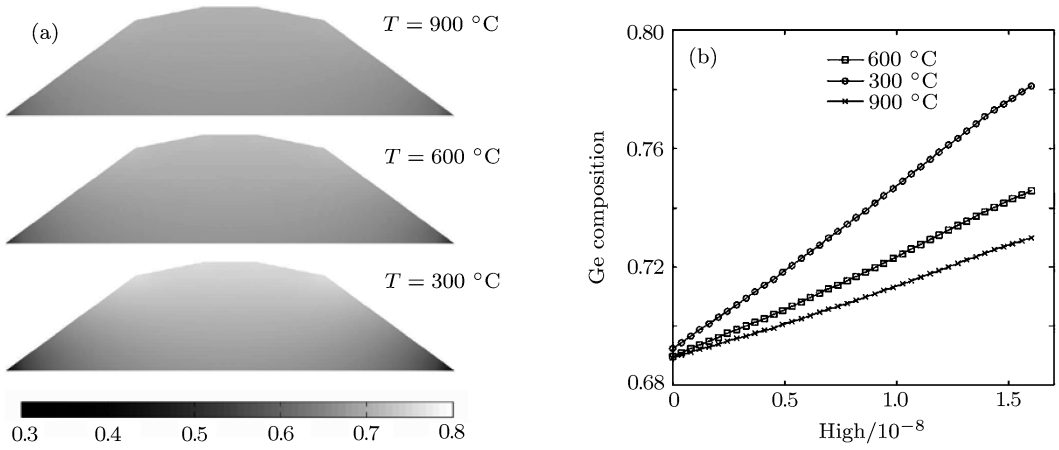


Fig. 2. Equilibrium composition of QD. (a) Equilibrium composition of QD at different temperatures; (b) Ge content along the vertical direction at the QD centre.

The contributions of different energies to equilibrium composition are also studied in this paper. The energies before and after optimization are computed for temperature 600 °C. The changes of three energies contributions are listed in Table 2. The main contribution to minimize free energy is from elastic energy, because the content of Ge increases at the top of the island and decreases at the bottom of it after optimization. This means that the lattice mismatch is minimized and the total elastic energy decreases evidently. Though the mixed energy is increased, the free energy could be minimized by elastic energy relaxation. So the elastic energy plays an important role in the QD formation.

Table 2. Energy change before and after optimization, the energies are given in units of 10^{-15} J.

	elastic energy	chemical energy	$-TS$	Gibbs free energy
before optimisation	1.338	1.943	–8.980	–5.699
after optimisation	1.280	1.932	–8.942	–5.730
change	–0.058	–0.011	0.038	–0.031

Figure 3 shows the decrease of free energy as a function of iteration. Only 20 iterations were needed for a satisfactory composition profile. And the evaluation of energy and sensitivity in iteration takes about 50 seconds. Our method is faster and simpler than the method invented by Uhl'ık.[10] So the method presented here is excellent in searching for the equilibrium composition by minimizing the free energy of QD.

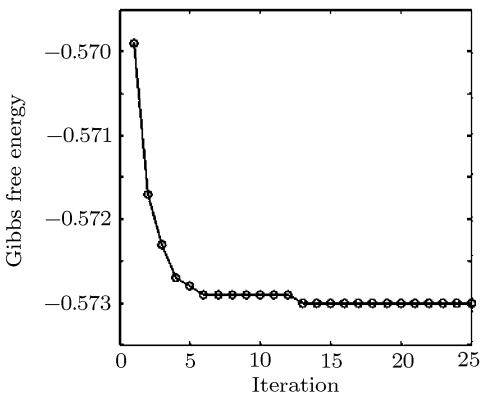


Fig. 3. The free energy as a function of iteration, the energy is given in units of 10^{-15} J.

The critical size of QD for transition between different shapes can be reduced by the effect of strain-induced segregation.[11] Finally, the influence of equilibrium composition to the critical size for shape transition of the pyramid-shaped Ge_xSi_{1-x} QDs (shown in Fig. 4.) is studied in this paper. The surface energy should be considered since it is important for the shape transition of QD. And it could be expressed as[30,31]

$$E_{\text{surface}} = (3V_{\text{q}})^{2/3} r^{-2/3} (\sqrt{1-4r^2} - 1)\gamma, \qquad (5)$$

where V_{q} is the volume of QD, r is the height-to-width aspect ratio of pyramid-shaped QD, γ is the surface energy density of QD ($\gamma = 2.22$ J/m^2 for GeSi). The

variation of the energy before and after optimization for QD with different interfacial angle ($\theta = 15°$ and $45°$ respectively) is shown in Fig. 5. When the QD has a uniform composition, the strain can be released more visibly in steep sidewall ($\theta = 45°$) than the flat one ($\theta = 15°$). And the surface energy is very large when the size of QD is small. The contribution to total energy from surface energy decreases when the size increases. The critical size for shape transition occurs when the gain from surface energy is smaller than the loss from elastic energy. The QD with the equilibrium composition has the minimum energy, which has the largest elastic energy relaxation. So the critical size for shape transition occurs at a smaller size after composition optimization.

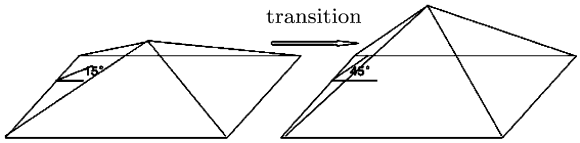


Fig. 4. Transition between pyramid-shaped QDs with different interfacial angles $\theta = 15°$ and $45°$.

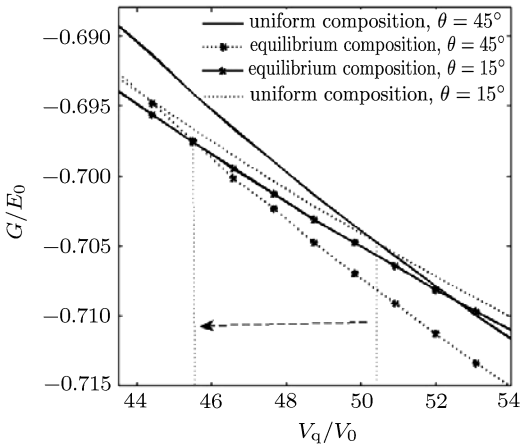


Fig. 5. The variation of the energy before and after optimization for QDs with different interfacial angles ($\theta = 15°$ and $45°$). The QDs have an average composition 0.5, characteristic volume[23] $V_0 = [\gamma/(M\varepsilon_{\rm m}^2)]^3$ and characteristic energy $E_0 = V_{\rm q}M\varepsilon_{\rm m}^2$($M\varepsilon_{\rm m}^2 = 2.82 \times 10^8$ J/m^3 for GeSi alloy).

4. Conclusions

In this paper, a fast method to search for the equilibrium composition of QD is presented, which based on MMA and sensitive analysis. A satisfactory optimization result can be obtained within 20 minutes, and agrees with other simulation methods.[10,11] The composition of Ge_xSi_{1-x}/Si QD at different temperatures is optimized. The entropy plays a major role in the contribution to Gibbs free energy at high temperatures. The mixing energy increases after optimization, but the free energy could be minimized by elastic energy's relaxation. The non-uniform composition profiles can be found at low temperatures, which agrees with the experimental results much better. The effect of composition on the critical size for shape transition of pyramid-shaped Ge_xSi_{1-x} QD is also studied in this paper, and the critical size will decrease when the effect of the composition of QD is introduced. The equilibrium composition of QD has the largest relaxation of elastic energy, which is the main reason for the decrease of the critical size.

Acknowledgments

We are grateful to Krister Svanberg for providing us with the matlab code for MMA algorithm.

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