Phase-Field Simulation of Self-Assembled Quantum Dots

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A phase-field model for self-assembled quantum dot formation has been developed in which the surface morphologies are determined to be dependent on the balance between the surface energy and the elastic strain energy caused by the lattice mismatch strain. The facet morphologies, which are often observed in semiconductor materials, have also been modeled using the generalized gradient correction coefficient for a crystal with a high anisotropy of surface energy. The variations of surface morphologies and energies have been examined by performing two-dimensional phase-field simulations for the annealing process of heteroepitaxial film. By taking sixteen-fold anisotropy into consideration, the multifaceted islands, which change shape with film thickness, can be created. The differences in morphological change and energy variations due to the mode number of the surface energy anisotropy have also been evaluated.

1. INTRODUCTION

The quantum dot formation in epitaxially grown thin solid films has been attracting much attention as a very promising area of nanotechnology that can lead to next-generation electronic devices 1). A typical size of quantum dots is in the range of 10 nm. The fabrication of these quantum dots on solid surfaces is beyond the capability of conventional lithography. Scanning probe microscopy techniques are under investigation as an alternative to the concept of optical lithography. Although they can achieve the atomic-scale nanostructures by manipulating single atoms, they are still very time-consuming. Recently, another approach for creating quantum dots based on the concept of pattern formation by self-assembly has drawn considerable attention. The self-assembly quantum dot formation is derived by elastic strain energy due to a lattice mismatch strain between the substrate and the thin film, and can realize a small size and a high density.

There are three possible heteroepitaxial growth modes, i.e., FM (Frank-van der Merwe) mode, VW (Volmer-Weber) mode, and SK (Stranski-Krastanov) mode. These growth modes are deduced from the equilibrium considerations of the energy balance between the surface energy, the interfacial energy, and the elastic strain energy associated with epitaxial lattice mismatch for heteroepitaxial systems. Some equilibrium phase diagrams, which can provide a detailed characterization of the possible growth mode, have been proposed by investigating the equilibrium properties of strained heteroepitaxial systems 2-4). To predict the equilibrium island shape and the morphological change during the growth process of quantum dots, however, numerical simulation is indispensable. Furthermore, a wide computational domain is necessary to examine the size distribution and array of yielded quantum dots. Therefore, atomic-scale simulations, such as molecular dynamics 5,6) and Monte Carlo 7), are difficult to apply.

In this study, a phase-field model for quantum dot formation is developed. The morphological change and the energy variation during the annealing process, where the thin film with a planar surface evolves into an island pattern, are clarified by conducting two-dimensional simulation 8), because we do not focus on the detail comparison with the previous experimental observations but on the stress...
relaxation mechanism caused by the surface morphological change. We introduce the generalized gradient correction coefficient for a crystal with a high anisotropy of surface energy to the phase-field model. As a result, the faceted island formation is possible \(^{(9-11)}\). It is well known that the stressed island forms a different shape from a stress-free one. For example, SiGe/Si heteroepitaxial systems show the \(\{105\}\)-faceted “hut” islands \(^{(12)}\) and the “dome” having \(\{105\}, \{15323\}\) and \(\{113\}\) facets \(^{(1)}\). Using the sixteen-fold of the surface energy, therefore, we try to create multifaceted islands, which change shape depending on film thickness.

2. PHASE-FIELD MODEL.

We consider a system composed of a substrate with a semi-infinite thickness, a thin film grown on the substrate heteroepitaxially and a vapor phase, which contact the thin film. The morphologies of the thin film are assumed to be determined by the competition of the surface energy and the elastic strain energy. The Ginzburg-Landau-type free-energy functional of the system is assumed to have the form

\[
F = \int \left[ f_\phi(\phi) + p(\phi) f_\phi(\phi, \varepsilon_{ij}) + \frac{a^2}{2} |\nabla \phi|^2 \right] dV
\]

where \(\phi\) is the phase field taking a value of 1 in the solid (= substrate + film) and 0 in the vapor phase, \(\varepsilon_{ij}\) is the strain tensor, and \(a\) represents the gradient correction coefficient. \(f_\phi(\phi)\) and \(f_\phi(\phi, \varepsilon_{ij})\) are the double-well potential and the elastic strain energy, respectively, and are defined by the following equations.

\[
f_\phi(\phi) = W\phi(\phi)
\]

\[
f_\phi(\phi, \varepsilon_{ij}) = \frac{1}{2} D_{ijkl}(\phi)(\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0)
\]

Here, \(W\) is the barrier height of the double-well potential \(G(\phi) = \phi^2(1 - \phi)^2\). \(\varepsilon_{ij}^0\) is the initial strain due to the lattice mismatch between the substrate and the thin film. \(D_{ijkl}(\phi)\) denotes the elastic coefficient, which takes 0 in the vapor phase and \(D_{ijkl}^0\) in the solid phase and varies continuously in the surface region. \(D_{ijkl}(\phi)\) is represented by

\[
D_{ijkl}(\phi) = \rho(\phi)D_{ijkl}^0
\]

where \(\rho(\phi)\) indicates the density of the solid phase \(^{(5)}\). We can change the distributions of the elastic coefficient by adjusting \(\tau\) in the following equation.

\[
\rho(\phi) = \frac{1}{2} \left[ \tanh \frac{2\phi - 1}{2\tau} + 1 \right]
\]

In Eq. (1), we chose \(p(\phi) = \phi^3(15\phi - 6\phi^2)\), which is a monotonically increasing function and satisfies \(p(0) = 0, p(1) = 1\), and \(p'(0) = p'(1) = 0\), where the prime denotes a derivative with respect to \(\phi\).

The surface anisotropy is taken into account using the following equation.

\[
a(\theta) = a_{s}\left[1 + \gamma \cos \theta \right]
\]

Here, \(a_{s}\) is a constant related to the surface energy \(\sigma\) and the surface thickness \(\delta\), \(\gamma\) is the strength of anisotropy, \(k\) is the mode number, and \(\theta\) is the angle between the surface normal and the \(x\)-axis. For values of high anisotropy such as \(\gamma > 1/(k^2 - 1)\), the polar plot of \(1:a_{s}\) is nonconvex when \(a + a_{s0} < 0\), where the subscript \(s\) denotes a derivative with respect to \(\theta\), and corresponding high-energy orientations are excluded from the equilibrium shape. The range of missing orientation is given by \((2\pi/k - \theta_m) < \theta < (2\pi/k + \theta_m)\), where \(i\) denotes integers from 0 to \(k-1\) and the corner angle of the equilibrium shape or the first missing orientation \(\theta_m\) is calculated from

\[
a(\theta_m)\sin \theta_m + a_{s}(\theta_m)\cos \theta_m = 0
\]

In order to provide the equilibrium morphology without so-called “ears” corresponding to the missing orientation, we use the regularized gradient correction coefficient for the region of the missing
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tation $^{(1)}$. 

$$a(\theta) = \begin{cases} a \left[ 1 + \gamma \cos k \theta \right] & \text{for } (2\pi/k + \theta_m) \leq \theta \leq (2\pi(k + 1)/k - \theta_m) \\ \frac{a(k)}{\cos \theta_m} \cos \theta & \text{for } (2\pi/k - \theta_m) < \theta < (2\pi/k + \theta_m) \end{cases} \quad (8)$$

The following time-dependent Ginzburg-Landau equations considering the effects of anisotropy can be obtained.

$$\frac{\partial \phi}{\partial t} = \nabla \left( MV \frac{\delta E}{\delta \phi} \right)$$

$$= MV^2 \left[ 2\phi(1-\phi)(1-2\phi)W + 30g(\phi) f_0(\phi, \epsilon) + \frac{\partial}{\partial x} \left( a \frac{\partial \phi}{\partial \theta} \frac{\partial \phi}{\partial y} \right) - \frac{\partial}{\partial y} \left( a \frac{\partial \phi}{\partial \theta} \frac{\partial \phi}{\partial x} \right) - a^2 \nabla^2 \phi \right] \quad (9)$$

Here, the phase field $\phi$ is assumed to be a conserved parameter. $M$ is the mobility representing the surface diffusion. We assume the stress equilibrium conditions $\sigma_{ij} = 0$, since the elastic relaxation occurs much faster than the surface diffusion.

The constants $a$ and $W$ are related to the surface energy $\sigma$ and the surface thickness $\delta$ by considering the one-dimensional steady-state condition $^{(3)}$.

$$a = \frac{3\delta \sigma}{b}, \quad W = \frac{6\sigma b}{\delta} \quad (10)$$

Assuming the surface region is $\lambda < \phi < (1-\lambda)$, we obtain

$$b = 2 \tanh^{-1}(1-2\lambda) \quad (11)$$

Since it is assumed that no morphological change of the substrate occurs, we set the term of the elastic strain energy in Eq.(9) to be strictly zero, or $f_0(\phi, \epsilon) = 0$, in the substrate.

3. NUMERICAL SIMULATION

The governing equations for phase field and stress field are discretized spatially using the finite difference method as a two-dimensional problem and the finite element method with isoparametric quadrilateral elements as a plane strain problem, respectively. We employ explicit time differencing on the phase-field equation.

![Computational model.](image)

Figure 1 shows the computational domain, boundary conditions and initial conditions. In Fig. 1, $t_s$ represents the substrate thickness and $t_f$ the initial film thickness. $dX$ and $dY$ are the length and width of the computational domain, respectively. The initial conditions for the phase-field variable are given by

$$\phi = \frac{1}{2} \left[ \tanh \left( \frac{b}{\delta} \left( y_{surf} - y \right) + 1 \right) \right] \quad (12)$$

where $y_{surf}$ indicates the $y$-coordinate of the initial surface of thin film. The initial surface is perturbed using the following equation.

$$y_{surf} = t_s + t_f + c dX \sum_{x=1}^{n} \sin \left( \frac{2\pi x}{dX} \times x \times 2\pi x \right) \quad (13)$$
Here, \( \chi \) is a random number distributed uniformly in the interval [0, 1], \( \alpha \) the amplitude and \( n \) the wave number.

The lattice mismatch strain \( \epsilon^{\text{mis}} \) in the thin film is expressed as \( \epsilon^{\text{mis}} = (a_f - a_s)/a_s \), where \( a_s \) and \( a_f \) are the lattice constants of the substrate and thin film, respectively. Since we assume that the substrate morphology does not change, it is convenient to apply the mismatch strain not to the thin film but to the substrate. The initial strain in the substrate is, therefore, set to \( \epsilon_{e_x}^0 = -\epsilon^{\text{mis}}_x \), and \( \epsilon_{e_y}^0 = 0 \) in the thin film.

When Eq.(9) is solved explicitly, a very small time increment \( dt < dx^4/\alpha^2 \lambda M \) and many time steps are required. Furthermore, the computational time for solving the stress field occupies most of the total CPU time. In order to conduct the simulation efficiently, therefore, some numerical techniques given below are introduced in the present simulations. Figure 2 illustrates the computational domains for phase-field and stress field. The phase-field equation, Eq.(9), is solved in the regions that include the vapor phase, the thin film and a part of the substrate. For the calculation of the stress field, the coarse meshes (9dx a side) are used in the substrate, which corresponds to the region in which the phase field is not solved, as shown in Fig. 2. In the vapor phase, the stress field is calculated only in the region in which the average value of the phase field in an element is larger than 0.1, because the stresses are zero in almost all of the vapor regions. The lattice size for solving the phase field equation is the same as the size of the finite element for the stress field. The stress field is calculated for a set number of steps. For the numerical results presented below in which a 3000000-step calculation is performed for the phase field, the stress field is solved every 100 steps until 1000000 steps, where the surface moves fast, and after the 1000000th step it is solved every 1000 steps.

We assume periodic boundary conditions for phase field at both sides, and fix the values \( \phi = 0 \) and \( \phi = 1 \) on the upper and lower ends, respectively. The displacements along the left-hand side and lower end of the computational domain are fixed in the \( x \) and \( y \)-directions, respectively. The displacement \( -dx \epsilon^{\text{mis}} \) is applied to the right-hand side of the domain, as shown in Fig. 2.

The following parameters are used in the present simulations, where the Si\(_{0.5}\)Ge\(_{0.5}\)/Si heteroepitaxial system is assumed: the length of the computational domain \( dx = 10.08 \mu m \), the width of the domain \( dy = 1.34 \mu m \), the size of the difference lattice and finite element \( dx = dy = 0.01 \mu m \), the substrate thickness \( t_s = 0.94 \mu m \), the film thickness \( t_f = 0.12 \mu m \), the surface energy \( \sigma = 1.23 \text{ J/m}^2 \) \(^{14}\), the surface thickness \( \delta = 4dx \), Young’s modulus \( E = 104 \text{ GPa} \) \(^{15}\), Poisson’s ratio \( \nu = 0.27 \) \(^{15}\), the lattice mismatch strain \( \epsilon^{\text{mis}}_x = 0.02 \), \( \lambda = 0.1 \), \( \tau = 0.1 \), \( \alpha = 0.01 \), and \( n = 100 \). The time increment \( dt \) is determined as \( dt = dx^4/(59.55\alpha^2 \lambda M) \) by taking the stability of numerical simulation into consideration. In the present simulations, we assume the isotropic elastic body and use the same physical properties in the thin film and substrate. Although we use Si\(_{0.5}\)Ge\(_{0.5}\)/Si system, in a wide range of Ge composition same morphological change has been observed. The main differences due to the composition are the size of the islands.

4. NUMERICAL RESULTS AND DISCUSSIONS

First, the results for the isotropic surface energy are represented. Figure 3 shows the time evolution of the surface morphologies, in which the surface is exhibited by the contour line of \( \phi = 0.5 \), and the stress distributions. Figure 4 indicates the variations of energy \( F_e \), \( F_s \), and \( F_c \); \( F \) is the total energy expressed by Eq.(1), \( F_e \) the elastic strain energy, and \( F_s \) the excess energy due to the presence of the surface, or \( F_s = F - F_c \). Figures 3 (a) - (e) correspond to those in Fig. 4. The morphological change and the energy variation can be roughly divided into four processes, which are denoted A, B, C and D in Fig. 4. Process “A” comprises the initial relaxation process and the quasi-steady process. After some steps, surface undulation is formed and a high stress concentration occurs around the valley of the surface undulation, as shown in Fig. 3 (b). The grooves generated from the valley of the surface undulation arrive at the film/substrate interface, and island morphologies are formed. The evolution of the grooves reduces to the rapid reduction of the elastic strain energy in process “B”. Although the surface energy \( F_s \), then, increases with surface area and curvature of the thin film, the total energy \( F \) decreases because the decrease in the elastic strain energy \( F_e \) is larger than the increase in \( F_s \). Under the condition illustrated in Fig. 3 (d), the subdividing process into the island morphologies is completed, and the energy varies slowly after this time. In process “C”, it is observed that the islands
with the complicated shape shown in Fig. 3 (d) slowly approach the half-circle shape. Finally, the steady-state condition "D" is achieved. It is observed that the final island density at the steady-state condition is less affected by the magnitude of initial surface perturbation.

Fig. 3  Time evolution of surface morphology and stress distribution $\alpha_s$ for isotropic surface

Next, we show the results taking the surface energy anisotropy into consideration. Here, we examine the two anisotropy modes $k = 4$ and $k = 16$. The four-fold anisotropy, $k = 4$, is widely used for the cubic structures. It is, however, well known that the shape of the stressed island is different from that of the stress-free crystal. For example, the SiGe/Si(100) island exhibits \{105\}-faceted "hut" islands and a "dome" having \{105\}, \{15 3 23\} and \{113\} facets. In the heteroepitaxy of the dilute alloy, the "barn" shape, in which steep \{111\} facets are introduced at the base of the \{113\} facets of the dome, has also been reported. We, therefore, adopt the anisotropy mode $k = 16$, or sixteen-fold anisotropy, in order to simulate the multifaceted island based on the similar idea of Ref. [17]. The introduction of the sixteen-fold surface energy anisotropy can determine the angles between the $x$-axis and the faceted surface, $\theta_x = 11.3^\circ$, $\theta_2 = 33.8^\circ$ and $\theta_3 = 56.3^\circ$, which are close to the angles between the $x$-axis and \{105\}, \{15 3 23\} and \{111\} facets, respectively. Figure 5 illustrates two-dimensional equilibrium shapes ($0 \leq \theta \leq \pi/2$) drawn using the Gibbs-Thomson equation and Wulf's theorem. Since the strengths of anisotropy employed here, or $\gamma = 0.1$ for $k = 4$ and $\gamma = 0.02$ for $k = 16$, are both larger than $1/(k^2-1)$, the drawings have so-called "cars" that do not belong to the equilibrium shape corresponding to the gray region. The first missing orientations $\theta_m$ are calculated to be $21.65^\circ$ and $9.35^\circ$ for $k = 4$, $\gamma = 0.1$ and $k = 16$, $\gamma = 0.02$, respectively.

Fig. 5  Equilibrium shapes ($0 \leq \theta \leq \pi/2$) with (a) $k = 4$, $\gamma = 0.1$ and (b) $k = 16$, $\gamma = 0.02$.

Figures 6 and 7 show the time evolutions of the surface morphologies and the stress distributions $\alpha_s$ for $k = 4$ and $k = 16$, respectively. For the case of $k = 4$, the surface is perturbed already at the 10000 steps as shown in Fig. 6 (a). The surface is composed of a lot of small triangular islands. With increasing number of steps, the island coalescence takes place and the islands become increasingly large. The formation process of the island morphology for $k = 4$, therefore, is different from the
isotropic case shown in Fig. 3. As for the case of \( k = 16 \), the processes of the morphological change shown in Fig. 7 are similar to the isotropic case shown in Fig. 3. Figure 8 shows the energy variations corresponding to the results of Figs. 3, 5 and 6 until 100000 steps. The results for the isotropy are the same as those shown in Fig. 4. Although it is shown that, in Fig. 4, the time evolution can be classified into four processes, for the results of \( k = 4 \) there is no process “A” and the total energy and the elastic strain energy almost linearly decrease with time at first. This difference in energy variation is considered to result from the difference in morphological change. In Figs. 3 and 7, the total energy rapidly decreases during groove growth, and this decrease in energy becomes slow after the groove reaches the film/substrate interface. On the other hand, for the case of \( k = 4 \) shown in Fig. 6, the morphological changes are continuous. Figure 8 shows the close-up views of equilibrium islands enclosed by broken line in Figs. 3, 6 and 7. The stress \( \sigma_x \) inside all islands shown in Fig. 8 is high around the film/substrate interface and becomes small directed upward. Tensile stresses occur in the substrate under the island, and the maximum stress is observed around the island base. The order of stress value and the stress distribution in islands are in good agreement with those represented by Ref. [18]. The island shape shown in Fig. 9 (c), or \( k = 16 \), represents the so-called “barn” type. In the present simulation, we have used a relatively large film thickness, because we focus on the strain relaxation mechanism caused by the surface morphological change: planar film to island morphology. If films thinner than those of the present simulations are used, other island shapes such as “hut” or “dome” can be created.

Fig. 6 Time evolution of surface morphology and stress distribution \( \sigma_x \) for anisotropic surface energy with \( k = 4 \) and \( \gamma = 0.1 \).

Fig. 7 Time evolution of surface morphology and stress distribution \( \sigma_x \) for anisotropic surface energy with \( k = 16 \) and \( \gamma = 0.02 \).

Fig. 8 Variations of total energy \( F_t \), surface energy \( F_s \) and elastic strain energy \( F_e \) for three conditions: isotropic surface energy, \( k = 4 \) and \( k = 16 \).

Fig. 9 Close-up views of islands enclosed by broken line in Fig. 3 (e), Fig. 6 (c) and Fig. 7 (c).

5. CONCLUSIONS

A phase-field model that can simulate the self-assembled quantum dot formation process has been
developed. In order to create the faceted island morphology, the technique using a regularized gradient correction coefficient is added to the model. We have demonstrated two-dimensional simulations for the annealing process of heteroepitaxial films. It is clarified that the transient process, in which the thin film with a planar surface changes to one with island morphologies, contributes to the decrease in total energy, which results from the competition between the decrease in elastic strain energy and the increase in surface energy. The morphological change process for the fourfold anisotropy differs from the case of isotropic surface energy. As a result, the variations of total energy also differ between the fourfold anisotropy and the isotropy. Furthermore, using sixteen-fold anisotropy, the multifaceted island can be simulated. We believe that the present phase-field model has a capability to reveal the more realistic and practical heteroepitaxial growth during deposition process.

REFERENCES