A thermodynamic theory of the self-assembly of quantum dots

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Abstract. We establish a general thermodynamic model to address the self-assembly of quantum dots (QDs) in heterogeneous epitaxial systems by taking into account the size-dependent surface and interface energies and the interactions between QDs. The proposed thermodynamic theory not only elucidates the growth mechanisms of the QD formation at a critical coverage and the physical origins of the narrow size distribution of QDs, but also predicts two important critical sizes in the QD growth: one is the critical size of the QD formation and the other is the critical size of the stable array of QDs. The theoretical results are in good agreement with the experimental observations, which implies that the established thermodynamic theory could be expected to be a general approach to pursue the physical mechanisms of self-assembly of QDs.
1. Introduction

In the last two decades, self-assembled quantum dots (QDs) have attracted considerable interest mainly because of their capability to confine electrons and holes in all spatial dimensions [1, 2]. Due to these unique properties, which resemble atomic-like behavior in condensed matter, QDs can be exploited for novel optoelectronic devices such as single-photon sources, lasers and optical amplifiers. Along these lines, key atomic-like features have been experimentally demonstrated in InAs/GaAs structures [3]–[5]. In experiments, researchers have intensively investigated the Ge/Si [6]–[9] and InAs/GaAs [10]–[13] systems and have shown that three-dimensional coherent islands can form after depositing a wetting layer and have a narrow size distribution. Meanwhile, the relevant theories [14]–[24] have been proposed for pursuing the physical mechanisms of the growth of QDs. However, the thermodynamic factors to determine the QD formation and the related QD array fabrication are not well understood yet [6, 18, 21].

Walther et al [23] and Cullis et al [24] experimentally measured the compositions of the QDs and wetting layer in the In$_x$Ga$_{1-x}$As/GaAs system using electron energy-loss imaging and presented the Walther, Cullis, Norris and Hopkinson (WCNH) mechanism that the Stranski–Krastanow (SK) epitaxial islanding transition is controlled by the strain due to the elemental segregation within the wetting layer. Therefore, this mechanism provides a good explanation for the SK growth mode and offers a new way of researching epitaxial systems exhibiting the SK transition. From the thermodynamic point of view, the driving force behind the growth of QDs is the gain in elastic relaxation energy on the top of islands on the basis of the above theories [14]–[22]. Generally, the gain in elastic relaxation energy $\Delta E_{\text{relaxation}}$ ($\Delta E_{\text{relaxation}} < 0$, which is proportional to the island volume $V$) counteracts the increase in surface energy $\Delta E_{\text{surface}}$ of islands (it is proportional to $V^{2/3}$). Obviously, when the volume of islands exceeds a certain value, the difference between the elastic relaxation energy and the surface energy $\Delta E$ ($\Delta E = \Delta E_{\text{surface}} + \Delta E_{\text{relaxation}}$) will be less than zero. That is, the formation of islands is more favorable thermodynamically.

However, this energetic theory brings a puzzle to us, i.e. we do not know why the islands cannot grow without limit. According to the above theories, the change in energy $\Delta E$ will decrease with increasing island volume, which shows that large islands are more stable than small ones [17], and there are no size limits for the stable island growth [21]. In order to explain...
the puzzle, the interactions between islands were taken into account [18, 20]. It was found that
the interaction energy can enhance the total energy of the system. Then, this energy increase
induced by interactions is not enough to alter the degression of the total energy of the system
(we will provide a detailed discussion of the issue in the following section). The main drawback
in the foregoing theories [14, 16, 19, 20] is that the surface energy of the wetting layer has been
considered to be invariable [17]. In fact, the surface energy of the wetting layer and the interface
energy between the wetting layer and the substrate are intimately related to the thickness of the
wetting layer.

For this issue, in this paper, we develop a general thermodynamic theory to address the
self-assembled growth of QDs in heteroepitaxial systems by taking the interactions between
QDs and the size-dependent surface and interface energies into account. We note that Müller
and Thomas [25] have given a theoretical analysis of the relationship between the surface energy
and thickness of the wetting layer. Therefore, in this work, the Müller and Thomas theory is
introduced into our model to calculate the surface energy of the wetting layer. Interestingly,
our theory distinctly answers why the island cannot grow without limit in the self-assembly of
QDs. Additionally, our thermodynamic theory not only elucidates the growth mechanisms of
QDs at a critical coverage and the physical origins of the narrow size distribution of QDs, but
also predicts two important critical sizes in the growth of QDs: one is the critical size of the QD
formation and the other is the critical size of the stable array of QDs. Importantly, the theoretical
results are in good agreement with the experimental observations [6]–[12], in which the critical
volume and the stable size of QDs and so on are consistent with our calculated results.

2. Thermodynamic theory

A schematic illustration of the self-assembly of QDs in a heteroepitaxial system is shown in
figure 1, in which the two situations A and B are constructed as shown in figure 1(a). Note

Figure 1. Schematic illustration of the islands’ shape and the islands’ array; 
$h_0$ and $h$ are the total deposited and the wetting layer thickness, respectively.
that the two situations have the same volume \( V \) and area \( S \). In situation A, a flat strain layer grows on the substrate without islands appearing. In situation B, coherent islands form after growing a wetting layer (the SK growth mode). The island array is considered to be located at the sites of an ideal hexagonal lattice \([26, 27]\), as shown in figure 1(b) in which all the islands have the same shape. In order to correspond to experiments \([6]–[11]\), these islands are pyramids when the volume is small, and then they are domes when the volume is large. Note that the small islands are square-based pyramids with four \([501]\) facets, while the large islands are multifaceted domes. The volume of layers in situation A is equal to the volume of the wetting layer and the islands, \( V_{(A)} = V_{(B)} \). In other words,

\[
Sh_0 = Sh + kV_D,
\]

where \( k \) is the number of islands on area \( S \), \( V_D \) is the volume of a single island, \( V_D = \frac{1}{3}t^3 \tan \theta \) or \( \frac{1}{2} \pi R^3 \tan \theta \) when the island is a pyramid or dome. The distance between the nearest-neighbor islands \( L \) can be written as \( L = \sqrt{2S/((2k)^3)} \).

We compare the total energy of the situations A and B, \( E_{(i)} \) \((i = A, B)\), which are given by \( E_{(i)} = E_{(i)\text{elastic}} + E_{(i)\text{surface}} + E_{(i)\text{interface}} \), in which \( E_{(i)\text{elastic}} \) is the elastic energy, \( E_{(i)\text{surface}} \) is the surface energy and \( E_{(i)\text{interface}} \) is the interface energy between the wetting layer and the substrate.

In situation B, the elastic energy includes the relaxation energy of islands \( (\Delta E_{\text{relaxation}} < 0) \), the strain energy of the wetting layer and the islands, and the interaction energy among islands. Thus, the total energy of situation B can be described as

\[
E_{(B)} = E_{(B)\text{strain}} + \Delta E_{\text{relaxation}} + E_{(B)\text{interaction}} + E_{(B)\text{surface}} + E_{(B)\text{interface}}.
\]

The elastic energy of situation A is equal to the strain energy of situation B, which can be written as \([28, 29]\), \( E_{(A)\text{elastic}} = E_{(B)\text{strain}} = 2G_l[(1 + \upsilon_l)/(1 - \upsilon_l)]f^2V \), in which \( V = V_{(A)} = V_{(B)} \). Therefore, the difference in total energy between situations A and B, \( \Delta E = E_{(B)} - E_{(A)} \), is

\[
\Delta E = \Delta E_{\text{relaxation}} + \Delta E_{\text{interaction}} + \Delta E_{\text{surface}} + \Delta E_{\text{interface}}.
\]

Accordingly, we can determine the growth mode (situation A or B) by comparing \( E_{(A)} \) with \( E_{(B)} \). If the total energy of situation A is less than that of situation B \((\Delta E > 0)\), the growth mode of situation A is energetically preferable. If the total energy of situation A is larger than that of situation B \((\Delta E < 0)\), the growth mode of situation B is energetically preferable. Additionally, we can determine the formation of the stable array of islands by calculating the minimum of \( \Delta E \).

In sections 2.1–2.3 we will deduce the analytical expressions of surface and interface energies, relaxation energy and interaction energy in equation (3), respectively.

2.1. Surface and interface energies

The surface energy of the wetting layer and the interface energy between the layer and the substrate are related to the thickness of the wetting layer. According to the Müller and Thomas theory \([25]\), if a few layers (the number of layers is \( n \)) are deposited on a substrate, the surface energy of the layer can be written as \( \gamma_1(n) = \gamma_1^\infty(1 - e^{-n/\xi}) \), in which \( \xi \) is a dimensionless parameter that depends on the interactions between layers, and \( \gamma_1^\infty \) is the surface energy of the semi-infinite solid whose material is the same as that of the layer. The interface energy
between the layer and the substrate is written as \( \gamma_{ls}(n) = (\gamma_1^\infty - \beta^\infty)(1 - e^{-n\xi}) + \gamma_s^\infty \) or \( \gamma_{ls}(n) = (\gamma_l^\infty - \gamma_s^\infty)(1 - e^{-n\xi}) + \gamma_s^\infty \), where \( \beta^\infty \) is the adhesion energy between the two semi-infinite solids (the material components are the same as that of the layer and the substrate), \( \gamma_s^\infty \) is the surface energy of the semi-infinite solid whose material is the same as that of the substrate, and \( \gamma_{ls}^\infty \) is the interface energy between the layer and substrate whose thicknesses are both infinite.

If we assume that the thickness of a monolayer is \( h_m \) and \( \psi \) is equal to \( h_m \xi \), the surface energy of the wetting layer with thickness \( h \) becomes

\[
\gamma(h) = \gamma_1^\infty (1 - e^{-h/\psi}).
\]  

(4)

The interface energy between the wetting layer and the substrate becomes

\[
\gamma_{ls}(h) = (\gamma_l^\infty - \gamma_s^\infty)(1 - e^{-h/\psi}) + \gamma_s^\infty.
\]  

(5)

In situation A, the surface energy is

\[
E_{(A)}^{\text{surface}} = \gamma(h_0)S = \gamma_1^\infty (1 - e^{-h_0/\psi})S
\]  

and the interface energy is

\[
E_{(A)}^{\text{interface}} = \gamma_{ls}(h_0)S = [(\gamma_l^\infty - \gamma_s^\infty)(1 - e^{-h_0/\psi}) + \gamma_s^\infty]S.
\]  

(7)

In situation B, the surface is divided into two parts: the surface of the wetting layer \((S - S_a)\) and the side faces of islands \((S_D)\). \( S_a \) is the area of the undersurface of islands \((S_a = kS_1)\); \( S_D = kS_1/\cos \theta \), where \( S_1 \) is the area of the single island base and is equal to \( \pi r^2 \) when the island is pyramid- or dome-shaped. Therefore, the surface energy can be written as

\[
E_{(B)}^{\text{surface}} = \gamma(h_1) (S - S_a) + \int_{S_D} \gamma_s dS,
\]  

(8)

where \( \gamma_s \) is the surface energy per unit area of the side faces of islands. When the island is pyramid-shaped, \( \gamma_s \) can be considered to be constant and is related to the tilt angle of the island surface, \( \theta \). Thus,

\[
\int_{S_D} \gamma_s dS = \gamma_s (\theta) S_D.
\]  

(9a)

In the case of large islands having a dome shape, the surface energy of islands is given by [22]

\[
\int_{S_D} \gamma_s dS = k \left( \gamma_0 (S_1/\cos(\theta)) + \frac{1}{\lambda} \int_{S_1/\cos(\theta)} \frac{1}{r} dS \right),
\]  

(9b)

where \( \gamma_0 \) is equal to the surface energy of pyramid-shaped islands, \( \lambda \) is the curvature energy that is determined largely by the bulk density and nature of the constituent species, and \( \frac{1}{\xi} \) is the local curvature of the surface area element \( dS \).

Similarly, the interface energy is divided into two parts, and the interface energy between the wetting layer and the substrate is written as

\[
E_{(B)}^{\text{interface}} = \gamma_{ls}(h) (S - S_a) + \int_{S_a} \gamma_s (h) dS,
\]  

(10)

where \( \gamma_s(h) \) is the interface energy per unit area of the undersurface of islands that depends on the distance \( h' \) between the side faces and the interface. Thus, when islands are pyramid-shaped, we get the second term of the above interface energy as follows:

\[
\int_{S_a} \gamma_s(h') dS = k \left[ G \left( \frac{-h}{\psi} \right) - G \left( \frac{h + t \tan \theta / 2}{\psi} \right) \right].
\]  

(11a)
where the function $G(\eta)$ is

$$G(\eta) = 4\psi \cot \theta \left[ \gamma_s^\infty (t + 2h \cot \theta) + \psi \gamma_{ls}^\infty \eta^2 \cot \theta + \left( \gamma_s^\infty - \gamma_{ls}^\infty \right) (t + 2h \cot \theta) e^\eta \right] + 2\psi \cot \theta \left( \gamma_s^\infty - \gamma_{ls}^\infty \right) (\eta e^\eta - e^\eta).$$  

(12)

When islands are dome-shaped, the second term of equation (10) is equal to

$$\int_{S_u} \gamma_u \left( h' \right) d\mathbf{S} = \pi k \left[ \gamma_{ls}^\infty R^2 + 2 \left( \gamma_s^\infty - \gamma_{ls}^\infty \right) \left( \frac{\psi}{\tan \theta} \right)^2 e^{-(h/\psi)} \left( e^{-R \tan \theta/\psi} + \frac{R \tan \theta}{\psi} - 1 \right) \right].$$

(11b)

2.2. Relaxation energy of islands

The relaxation energy of a single island has been well studied [30]–[33]. It is recognized that the relaxation energy of a single island is related to the shape of the island and the elastic constants of the island and the substrate. Thus, we can simply write the relaxation energy as

$$\Delta E_{\text{relaxation}} = -E R V D,$$

in which $E$ is the elastic factor between the island and the substrate, and $R$ is the shape factor of the island.

In our studies, we use the Tersoff and Tromp model [31] to calculate the relaxation energy of pyramids. In this model, the relaxation energy of a single island can be written as

$$\Delta E = -\frac{9}{2} c V_D \tan \theta,$$

in which $c = (M_i \varepsilon)^2 (1 - \nu_s)/2\pi G_s$. Additionally, $M_i$ and $\varepsilon$ are Young’s modulus and the misfit strain of the island, and $\nu_s$ and $G_s$ are Poisson’s ratio and the shear modulus of the substrate. Accordingly, the total relaxation energy of all the islands in the area $S$ is

$$\Delta E_{\text{relaxation}} = -\frac{9}{2} c V_D \tan \theta.$$  

(13a)

According to our previous work [30], the relaxation energy of a dome-shaped island can be given by

$$\Delta E = -\frac{9}{\sqrt{\pi}} c V_D \tan \theta.$$  

(13b)

2.3. Interaction energy among islands

The elastic interaction energy between two islands ($i$ and $j$) with the same shape and volume can be written as [20]

$$E_{ij} = \frac{1 + \nu}{1 - \nu} \frac{Y}{\pi} \frac{1}{r^3} \int_{V_i} dV \int_{V_j} dV' \frac{1}{r^3},$$

where $\nu$ and $Y$ are Poisson’s ratio and Young’s modulus of the islands, and $r$ is the distance between $dV$ and $dV'$. Thus, the elastic interaction energy among all the islands in the area $S$ is

$$E_{\text{interaction}} = \sum_i \sum_{i \neq j} E_{ij} = \frac{1}{2} k \sum_{j=2}^k E_{1j}.$$  

(14)

If the distance between islands is much larger than the diameter of the island ($L \gg t$ or $L \gg 2R$), the interaction energy can be approximately written as

$$E_{ij} = \frac{1 + \nu}{1 - \nu} \frac{Y}{\pi} \frac{1}{L^3}.$$

(15)
Calculated from equation (16)
Calculated from equation (15)

Figure 2. Interaction energy calculated according to equations (15) and (16).

For the dome-shaped islands, the elastic interaction energy between two islands can be written as [14]

$$E_{ij} = \frac{1 + \nu}{1 - \nu \pi} Y \epsilon^2 \nu_D^2 \frac{1}{L^3} F\left(\frac{\rho}{L}\right), \tag{16}$$

where \(\rho = (3\pi^{-1}\cot \theta V_D)^{1/3}\) and \(F(\rho/L)\) is the correction factor that equals

$$F\left(\frac{\rho}{L}\right) = \sum_{s=0}^{\infty} \left\{ \sum_{p=0}^{s} \frac{(\rho/L)^s}{\Gamma(p+1) \Gamma(s-p+1)} \right\} \frac{9}{4 (p+1) (p+3/2) (s-p+1) (s-p+3/2)} \times \left[ \frac{\Gamma(3/2+s)}{\Gamma(3/2)} \right]^2. \tag{17}$$

Figure 2 shows the calculated results according to equations (15) and (16). Note that the volume of the island is 1000 nm\(^3\) and the contact angle is 11.3° in our calculations. Clearly, we can see that the two values of the interaction energy have an obvious difference when the two islands are close to each other. However, the interaction energies become almost equal and close to zero with increasing distance. Therefore, we can calculate the interaction energy using equation (15) for the small islands, because the distance \(L\) is much larger than the size of the island, \(t\), and using equation (16) for the large dome-shaped islands, respectively. Note that we neglect the deformation within the wetting layer due to the presence of islands, because the deformation energy induced by islands is too low in the case of the small islands, and much weaker than the interaction energy in the case of the large islands due to the small surface area and low thickness of the wetting layer. Furthermore, in our calculations, we just consider the interactions between islands with nearest neighbors whose distance is \(L\) and number is six, the next nearest neighbors whose distance is \(\sqrt{3}L\) and number is six and the third-nearest neighbors whose distance is \(2L\) and number is six, as shown in figure 1(b).
3. Results and discussions

3.1. Results

We separate the island growth process into two phases: one is the formation phase in which the three-dimensional pyramid islands form on the wetting layer and the other is the growth phase in which the islands grow from pyramids to domes until they achieve thermodynamic equilibrium. Definitely, the formation phase determines the island density \[ k \] and the minimum size of islands. In the second phase, we can get the size of the stable islands by calculating the minimum of the total energy \( \Delta E \). In our calculations, we assume that the area is \( S = 1 \mu m^2 \) and analyze the values of \( \Delta E \) with a change in the volume of islands \( V_D \) and the island density \( k \). The value of the area \( S \) that we set in our model has no influence on our theoretical results, because we can set the different island densities by altering the number of islands \( k \). Now, we take the Ge/Si (001) system as an example to study how the established theory operates in the formation of QDs.

For the Ge/Si(001) system, the constant \( c = 0.27 \text{ eV nm}^{-3} \) [21], the misfit strain is \( \varepsilon = 0.042 \), and Poisson’s ratio and Young’s modulus of Ge are 0.273 and 103 GPa, respectively [34]. The surface energies of Ge and Si are 10.4 and 11.8 eV nm\(^{-2}\), respectively [35]. The parameter \( \psi = 0.28 \text{ nm} \) [25]. In our calculations, the interface energy between bulk materials, i.e. \( \gamma_{ls} \), is ignored.

Figure 3 shows the results of the formation phase of small pyramid-shaped islands. Clearly, we can see that the total energy rises with increasing volume of islands initially, and then the total energy starts to decrease when the volume reaches a certain value, which is called the second critical volume \( V_C \), as mentioned in [21]. When the difference in total energy \( \Delta E \) between two situations drops below zero with increasing volume, the growth mode of situation B is energetically preferable, and the created islands of small size can grow steadily. We call the volume the first critical volume \( V_C \) when the difference in total energy \( \Delta E \) is zero. Figure 3(a) shows the change in \( \Delta E \) with increasing volume of islands under the condition \( h_0 = 2.5 \text{ nm} \).
Figure 4. (a) Total energy as a function of island size (domes) in the Ge/Si(001) system under different island densities and a fixed deposited $h_0 = 2.0$ nm. (b) Total energy change with increasing island volume for two types of island shapes: pyramid and dome.

Based on this result, we can see that there are nearly the same critical volumes for the different densities. In figure 3(b), we show the change in $\Delta E$ with increasing volume of islands for a fixed island density under the conditions $k = 100$ and $h_0 = 1.0, 1.3, 1.5, 2.0$ and $2.5$ nm, respectively. Definitely, it is impossible to form islands when the total deposited $h_0$ is too small, which means that situation A is favorable at the beginning stage of growth, and the islands can only form on the wetting layer when the wetting layer reaches a certain thickness. All the analytic results show that the growth process is the typical SK growth mode, in which the islands can form only at a critical coverage. Importantly, these theoretical results are in good agreement with the experimental observations [6]–[9]. Figure 3(a) shows the first critical volumes for different $h_0$ and $k = 100$. The critical volumes are larger than 550 nm$^3$. That is, the island diameter $t > 25$ nm. Interestingly, these results are consistent with the experimental observations [6], in which the small islands whose diameter is smaller than a critical value (about 30 nm) are unsteady and maybe disappear instead by a wetting layer, but the large islands whose volume is above the critical volume can grow rapidly until they reach a steady size.

The islands cannot grow without limit when the volume of islands exceeds the critical volume under the condition of a fixed island density and total deposited $h_0$. The interaction energy among islands and the size-dependent surface and interface energies restrict the growth of islands. Therefore, these islands will reach a steady state when they grow to a certain volume. We calculate the change in $\Delta E$ with increasing volume of islands under the condition of fixed $k$ and $h_0$. Figure 4(a) shows the calculated results of the second phase where the islands are considered to be dome-shaped when $h_0 = 2.0$ nm and $k = 80$, 100, and 120. We note that the steady volume decreases with increasing island density. In fact, this is because the amount of material deposited is given by the size-dependent surface energy and the interactions among islands are more effective for the higher island density. Therefore, these theoretical results explain well why the islands have a narrow size distribution. In [6, 7], the island density is about $80 \mu m^{-2}$. Then, our calculated results show that the island diameter and the volume of the steady state are 60–75 nm and 8 000–15 000 nm$^3$, respectively, under the condition of an island density of $80 \mu m^{-2}$ and the total deposited $h_0$ in the range of 1.5–2.0 nm. Accordingly, these theoretical results are in good agreement with the above experimental data.
Table 1. The related parameters used in our calculations.

|                 | Surface energy (eV nm\(^{-2}\)) | Young’s modulus (GPa) | Poisson’s ratio |
|-----------------|----------------------------------|-----------------------|----------------|
| InAs            | 8.75 [36]                        | 51.4 [37]             | 0.35 [37]      |
| GaAs            | 13.75 [36]                       | 86.3 [38]             | 0.31 [38]      |

Figure 5. The first critical volume of islands as a function of the total deposited \(h_0\) under a fixed island density \(k = 100\) in the Ge/Si(001) system as shown in (a) and in the InAs/GaAs(001) system as shown in (b). The insets in (a) and (b) show the relationship between the second critical volume and the total deposited \(h_0\).

in which the diameter of the steady island is about 50–70 nm [6] and the volume is about 10 000–20 000 nm\(^3\).

In the growth phase, the shape transition from pyramid to dome can take place before the islands reach a steady state. Figure 4(b) shows the total energy change as a function of island volume for the two different shapes. We note that the energy of the dome islands is higher than that of the pyramid islands in the case of small volumes, while it is the opposite case with increasing volume. This result suggests that the pyramid islands form in the early stages, and then the shape transition happens when the volume exceeds a certain value. The volume of the shape transition \((V_T)\) is calculated to be about 4000 nm\(^3\), i.e. the diameter is about 50 nm, as shown in figure 4(b). These results are consistent with the experiments [6, 7, 9], in which the diameter of the shape transition is about 40–50 nm.

The proposed thermodynamic theory is also applicable to the InAs/GaAs(001) system. Table 1 lists the related parameters used in our calculations. The shear modulus of GaAs is 32 GPa, which is calculated by Young’s modulus \(Y\) and Poisson’s ratio \(\nu\) as follows: \(G = Y/2(1 + \nu)\). Figure 5(b) shows the calculated results of the formation phase of islands. We can see that the first critical volume is larger than 300 nm\(^3\), i.e. \(t > 20\) nm, and the second critical volume is larger than 80 nm\(^3\), i.e. \(t > 13\) nm. In fact, the critical volume in the InAs/GaAs(001) system is reported experimentally to be larger than that of the Ge/Si(001) system [10, 11]. Nakata et al [10] reported that the diameter of the smallest island is about 20 nm, and Joyce et al [12] reported that the width of the typical InAs QD is 25 nm, which is in good agreement.
with our calculated results. Additionally, we need to point out that smaller islands have been observed [11]. In other words, the initial InAs QDs have an average diameter of 12.5 nm [11], which is coincident with our calculated second critical volume.

The first and second critical volumes in the formation phase of islands have different physical significance. The islands with volumes larger than the first critical volumes mean that the growth mode of the islands has a lower energy and is more favorable than that of the layer-by-layer mode, and the islands cannot disappear with increasing volume or annealing. When the volume of islands is between the second critical volume and the first critical volume, the islands can grow steadily due to the total energy decreasing with increasing volume. However, the islands have two evolution routes during annealing at high temperatures: one is that the islands shrink and disappear when the islands are above the energy barrier, and the other is that the islands keep the former size or grow at the expense of the wetting layer. Thus, it is understandable that islands with smaller size than the first critical volumes in the deposited process are observed in experiments [11].

3.2. Discussion

We take the Ge/Si(001) system as an example to discuss the influence of the size-dependent surface and interface energies and the interaction energy on the formation and growth of islands.

In the formation phase of the growth of islands, the interaction energy can be ignored because the volume of islands is small and the relative distance between islands is large. Therefore, the island density is not effective for the island formation as shown in figure 3(a), in which there are nearly the same critical volumes for different densities. The size-dependent surface and interface energies influence intensively the forming ability of islands. For island situation A, i.e. before the islands form, the total surface and interface energies can be written as $\gamma_{\text{total}} = \gamma_1^\infty + (\gamma_s^\infty - \gamma_l^\infty) e^{-h/\psi}$ according to equations (9) and (10) if we ignore the interface energy between bulk materials. The value of $h/\psi$ determines the total surface and interface energies, which are $\gamma_{\text{total}}(h/\psi \to \infty) \to \gamma_1^\infty$ and $\gamma_{\text{total}}(h/\psi \to 0) \to \gamma_s^\infty$. Since $\gamma_s^\infty > \gamma_1^\infty$ for the SK growth mode, the influence of the size-dependent surface and interface energies becomes weak with increasing thickness of the layer as shown in figure 3(b), in which the critical volume of islands becomes small with increasing $h_0$. Thus, this result shows that the formation ability of islands becomes strong. Figure 6 shows the influence of different values of $\psi$. The smaller the values of $\psi$ are, the stronger the formation ability of islands. If we neglect the size-dependence of the surface and interface energies, namely, $\gamma_1(h) = \gamma_1^\infty$ and $\gamma_s(h) = 0$, the islands can form under the condition of any thickness of the layer as shown by the dashed line in figure 6, which is not consistent with the SK growth mode. All these results not only give an explanation as to why the islands can form only at a critical coverage, but also show that it is necessary to consider the size-dependence of the surface and interface energies in the formation phase of the growth of islands.

In the growth phase of islands, the interaction energy becomes significant because of the large volume of islands and the small distance between islands. In this phase, the wetting layer $(h)$ becomes thin when the islands grow for a fixed $h_0$. Thus, the size-dependent surface and interface energies are effective for the islands’ growth. In figure 7, we show the various energy contributions to the islands’ growth. The interaction energy and the size-dependent surface and interface energies have negative effects on the islands’ growth and restrict the islands.
Figure 6. The critical volume of islands as a function of the total deposited $h_0$ under different values of the parameter $\psi$ in the Ge/Si(001) system.

Figure 7. Various energy contributions of the interaction energy, the relaxation energy and the size-dependent surface and interface energies to the growth of islands under $k = 100$ and $h_0 = 2.0$ nm. The dashed line indicates the contributions of surface and interface energies whose size-dependence is ignored.

from infinite growth. Therefore, we can see that the contribution of interactions cannot alter the degression of the total energy. In the second phase of the growth of the islands, the thickness of the layer becomes small when the islands grow for a fixed $h_0$. Thus, the main negative effect is the size-dependent surface and interface energies that become large with decreasing thickness of the wetting layer. Therefore, the total energy will rise when the volume of islands exceeds a certain value. Clearly, there is a steady state with minimum total energy.
4. Conclusion

We have proposed a general thermodynamic model to analyze the formation and growth of coherent islands, in which the interactions among islands and the size-dependence of surface and interface energies are taken into account. Theoretical results not only explain why the islands can form only at a critical coverage and why the islands cannot grow without limit, but also predict the critical size of the formation of islands and the stable array of QDs. Theoretical predictions are consistent with experiments, which suggests that the established thermodynamic approach could be expected to be applicable to understand self-assembly of QDs.

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