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A kinetic study of the ordering process in ternary III–V semiconductor alloys

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Abstract. In the epitaxial growth of ternary III–V semiconductor alloys, the microscopic diffusion theory is applied to studying the effect of surface reconstruction and the influence of sublayer atomic diffusion on the CuPt-type ordering process. It is found that the on-site energy induced by reconstruction plays a central role in the kinetic process of the surface ordering. In view of the kinetics it is demonstrated that the surface ordering is frozen in after subsequent coverage and the sublayer diffusions have little influence on the ordering of the alloy. Consequently, two variants of CuPt-type ordering are obtained through layer-by-layer stacking. Moreover, during the sublayer ordering process, the order of the sublayer is shown to transiently overshoot the equilibrium order. The ordering kinetics in the order–disorder heterostructure is also investigated by considering the effects of growth temperature.

1. Introduction

The phenomenon of spontaneous long-range ordering in ternary III–V semiconductor alloys has been widely observed during epitaxial growth and intensively studied [1–11]. The ordering is known to significantly influence the fundamental properties of the materials and be useful for application in optoelectronic devices. For epitaxial growth on a (001) substrate, the most commonly observed ordered structure is type CuPt ($L1_1$), and only two of four variants are found with the ordering along the $[1\bar{1}1]$ and $[\bar{1}11]$ directions [1–6]. Recently, a GaInP order–disorder heterostructure has been grown which is composed of adjacent completely disordered and highly CuPt-type ordered materials [7], and the growth of a GaInP disorder–order–disorder quantum well structure has also been reported [8].

Many experimental and theoretical researches show that surface reconstruction plays an important role in the formation of ordered phase [2, 4, 9–11]. In both $A^{\text{III}}B^{\text{III}}C^{\text{V}}$ -type and $C^{\text{III}}A^{\text{V}}B^{\text{V}}$ -type ordered alloys the appearance of surface reconstruction has been reported, such as the (2×1) reconstruction in AlInAs [9], the (2×4) reconstruction in GaAsSb [2], and the (2×3) reconstruction in InAsSb [4]. The first-principles total-energy calculations and the thermodynamic calculations based on the cluster-variation method demonstrated that the surface reconstruction stabilizes the observed CuPt-type variants in the GaInP alloy [10, 11]. Moreover, a frozen surface ordering model was proposed to explain the appearing three-dimensional CuPt-type ordered structure [11]. The model supposes that the ordering takes place at the growing surface due to surface reconstruction, and when the surface is covered by subsequent layers, the surface ordering is frozen in because of the insufficient very low bulk diffusion.

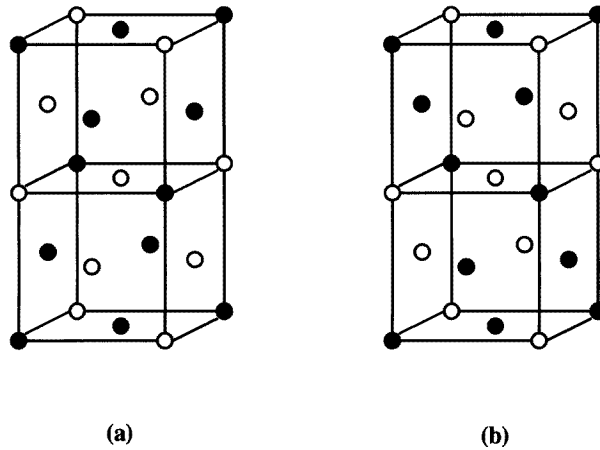


Figure 1. Two observed variants of CuPt-type long-range ordered structures (only the ordered fcc positions are shown). (a) $1/2L1_1[1\bar{1}\bar{1}]$ and (b) $1/2L1_1[\bar{1}11]$.

Since in the epitaxial growth the layer-by-layer stacking process is a kinetic phenomenon, the ordering mechanism could be explained more clearly through a kinetic study. One type of kinetic model to describe the order–disorder process is the microscopic diffusion theory [12, 13], which is the microscopic counterpart of the well known Cahn–Hilliard equation [14]. This theory has been used to describe many important processes, such as ordering, decomposition, clustering and coarsening [15, 16]. Numerical simulations of the structural transformation based on this kinetic theory have been performed on a two-dimensional square lattice to study the ordering and decomposition processes [15]. Recently, Chen discussed this microscopic theory in detail and used it to describe the order–disorder kinetics in binary alloys with bulk bcc or two-dimensional square lattices [16].

We use this kinetic theory to study the CuPt-type order–disorder processes of the top surface, the subsequent layer-by-layer stacking, and the order–disorder heterostructure. The nearest-neighbour intralayer and interlayer interactions and diffusions are considered in our study. We find that the on-site energy induced by the reconstruction plays a central role in the surface ordering and the stacking process. We also show from the kinetic equations that the growth temperature has important influences on the order–disorder process, such as the process of the formation of order–disorder heterostructure, and the surface ordering can be really frozen in. Moreover, a overshooting effect occurs during the sublayer ordering process.

In section 2, the kinetic equations for the surface ordering and sublayer ordering are derived. We show the results on the ordering process in section 3. The conclusion is presented in section 4.

2. Kinetic equations of the ordering process

In ternary III–V semiconductor alloys, $A^{\text{III}}B^{\text{III}}C^{\text{V}}$ or $C^{\text{III}}A^{\text{V}}B^{\text{V}}$, ordering of atoms A and B occurs on one set of fcc positions, and atoms C fully occupy the other set of fcc positions. Figure 1 presents two observed variants of CuPt-type ordered structure, where only the ordered fcc positions are shown. Therefore, we may study only the layers occupied by atoms A and B.

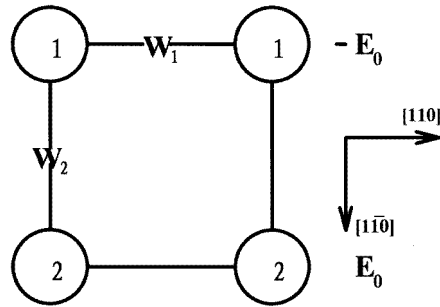


Figure 2. Two-dimensional surface layer structure in (001) substrate growth. The atomic sites are divided into two sublattices 1 and 2. W_1 and W_2 are the nearest-neighbour interactions, and E_0 is the on-site energy.

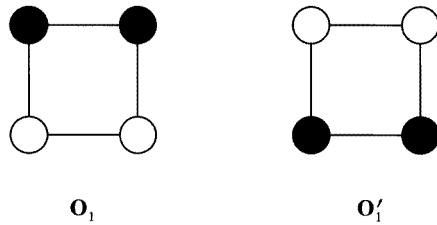


Figure 3. Two equivalent planar ordered structures O_1 and O'_1 corresponding to three-dimensional CuPt-type structure.

The two-dimensional surface structure is shown in figure 2, where the atomic sites belong to the set of fcc positions occupied by atoms A and B, and are divided into two sublattices 1 and 2. W_1 and W_2 are the nearest-neighbour interaction, and usually $W_1 \neq W_2$ due to the influence of atoms C below the layer occupied by atoms A and B. E_0 is the on-site energy introduced in [11] for the first-principles total-energy calculations of epitaxial layers in the GaInP alloy, which reflects the effects of local strains induced by surface reconstruction and is present only in the reconstructed case. Here we consider a reconstructed surface terminated by atoms A and B. We choose that $-E_0$ is the on-site energy on sublattice 1 and E_0 is that on sublattice 2, since we only consider the kinetic process between the disordered and CuPt-type ordered phases. The two equivalent planar ordered structures O_1 and O'_1 corresponding to three-dimensional CuPt-type phase are shown in figure 3.

The kinetic equation of microscopic diffusion theory for several interpenetrating Bravais lattices is [12, 13]

$$\frac{dp_i(\mathbf{r}, t)}{dt} = \sum_{i'} \sum_{\mathbf{r}'} \frac{c(1-c)}{k_B T} L_{ii'}(\mathbf{r} - \mathbf{r}') \frac{\delta F}{\delta p_{i'}(\mathbf{r}', t)} \quad (1)$$

where $p_i(\mathbf{r}, t)$ is the occupation probability for atom B at site \mathbf{r} on sublattice i at time t , $L_{ii'}(\mathbf{r} - \mathbf{r}')$ is the diffusion jump coefficient from site \mathbf{r} on sublattice i to site \mathbf{r}' on sublattice i' , c is the composition for atom B of the layer occupied by atoms A and B, F is the free energy of the system, T is the temperature, and $\delta F / \delta p_i(\mathbf{r}, t)$ represents the functional derivative of F with respect to $p_i(\mathbf{r}, t)$.

For the two-dimensional surface structure, the mean-field free energy F can be written

as

$$F = -E_0 \sum_{\mathbf{r}} p_1(\mathbf{r}) + E_0 \sum_{\mathbf{r}} p_2(\mathbf{r}) + \frac{1}{2} \sum_{ii'} \sum_{\mathbf{r}\mathbf{r}'} W_{ii'}(\mathbf{r} - \mathbf{r}') p_i(\mathbf{r}) p_{i'}(\mathbf{r}') \\ + k_B T \sum_i \sum_{\mathbf{r}} [p_i(\mathbf{r}) \ln p_i(\mathbf{r}) + (1 - p_i(\mathbf{r})) \ln(1 - p_i(\mathbf{r}))] \quad (2)$$

where $i, i' = 1, 2$ and $W_{ii'}(\mathbf{r} - \mathbf{r}')$ is the effective interaction between site \mathbf{r} on sublattice i and site \mathbf{r}' on sublattice i' .

In this work we only consider the nearest-neighbour interactions W_1 and W_2 , as well as the nearest-neighbour diffusions. We have studied the kinetic properties by considering the higher-neighbour terms in further work, and the main results are the same as those in the nearest-neighbour approximation. We assume that the occupation probability for atom B at each site of sublattice 1 is p_1 , that for atom B at each site of sublattice 2 is p_2 , and then the composition of the layer $c = (p_1 + p_2)/2$. Therefore, if the composition c is $\frac{1}{2}$, we have $p_1 + p_2 = 1$. The long-range order parameter of the CuPt-type ordering can be defined as $\eta = p_1 - p_2$. Thus, from (1), we have

$$d\eta/dt = dp_1/dt - dp_2/dt = \frac{1}{k_B T} \left[(L_{11} - L_{21}) \frac{\delta f}{\delta p_1} + (L_{12} - L_{22}) \frac{\delta f}{\delta p_2} \right] \quad (3)$$

where $L_{ii'}$ ($i, i' = 1, 2$) is the nearest-neighbour diffusion coefficient from sublattice i to i' , and $f = F/N$, N is the total number of the sites in the whole layer, that is, on both sublattices 1 and 2. Because of the symmetry of diffusion coefficient $L_{ii'}$, we assume

$$L_{21} - L_{11} = L_{12} - L_{22} = L. \quad (4)$$

Thus, from (2) and (3), we obtain the kinetic equation of the surface ordering process:

$$\frac{d\eta}{d\tau} = e + a\eta + \ln \frac{1 - \eta}{1 + \eta} \quad (5)$$

where

$$e = E_0/k_B T \\ a = (W_2 - W_1)/k_B T \\ \tau = Lt. \quad (6)$$

During the epitaxial growth process, the top surface is buried by the subsequent layer and becomes the sublayer. To study the formation of three-dimensional ordered structure, the nearest-neighbour interaction and atomic diffusion between the surface layer and the sublayer should be considered.

In figure 4, the surface layer and the sublayer are labelled as layer 0 and layer 2, respectively, and refer to the layers occupied by atoms A and B. The sites in these two growth planes are considered to be composed of two sublattices, 1 and 2. W_1^n and W_2^n ($n = 0, 2$) are the nearest-neighbour interactions in layer n , and W_{02} is the nearest-neighbour interlayer interaction. The occupation probability for atom B is denoted as p_i^n in layer n ($n = 0, 2$) on sublattice i ($i = 1, 2$). We can write the free energy $f = F/N$ as

$$f = \frac{E_0}{2} (-p_1^0 + p_2^0) + \frac{E_2}{2} (-p_1^2 + p_2^2) + \frac{1}{2} \sum_{ii'} \sum_{nn'} W_{ii'}^{nn'} p_i^n p_{i'}^{n'} \\ + k_B T \sum_{in} [p_i^n \ln p_i^n + (1 - p_i^n) \ln(1 - p_i^n)] \quad (7)$$

where E_2 denotes the on-site energy of the sublayer induced by the top-surface reconstruction, and $W_{ii'}^{nn'}$ denotes the nearest-neighbour interaction (W_1^n , W_2^n or W_{02}).

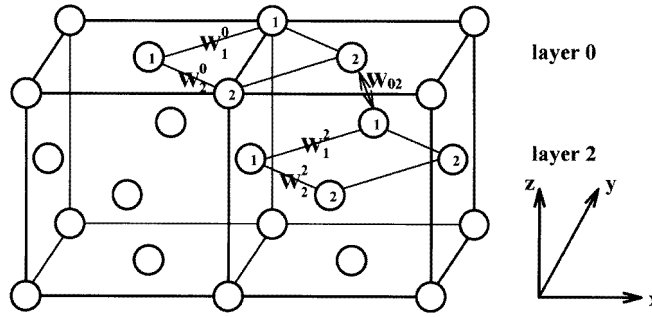


Figure 4. Three-dimensional structure of the alloy in (001) substrate growth (only the ordered fcc positions are shown). The surface is labelled as layer 0 and the sublayer is labelled as layer 2. Two sublattices 1 and 2 are labelled on the atomic sites. W_1^n and W_2^n ($n = 0, 2$) denote the nearest-neighbour interactions in layer n , and W_{02} is the nearest-neighbour interlayer interaction.

We define the long-range order parameter in layer 0 and 2 as $\eta_0 = p_1^0 - p_2^0$ and $\eta_2 = p_1^2 - p_2^2$, respectively, and the diffusion coefficient from layer n on sublattice i to layer n' on sublattice i' as $L_{ii'}^{nn'}$. Substituting (7) into (1) for $c = \frac{1}{2}$, we obtain the kinetic equations for the surface layer and sublayer ordering:

$$\frac{d\eta_0}{dt} = L^{00} \left(\frac{E_0}{k_B T} + \frac{W_2^0 - W_1^0}{k_B T} \eta_0 + \ln \frac{1 - \eta_0}{1 + \eta_0} \right) + L^{02} \left(\frac{E_2}{k_B T} + \frac{W_2^2 - W_1^2}{k_B T} \eta_2 + \ln \frac{1 - \eta_2}{1 + \eta_2} \right) \quad (8)$$

and

$$\frac{d\eta_2}{dt} = L^{20} \left(\frac{E_0}{k_B T} + \frac{W_2^0 - W_1^0}{k_B T} \eta_0 + \ln \frac{1 - \eta_0}{1 + \eta_0} \right) + L^{22} \left(\frac{E_2}{k_B T} + \frac{W_2^2 - W_1^2}{k_B T} \eta_2 + \ln \frac{1 - \eta_2}{1 + \eta_2} \right) \quad (9)$$

where $L^{nn'}$ ($n, n' = 0, 2$) is defined as

$$L_{21}^{nn'} - L_{11}^{nn'} = L_{12}^{nn'} - L_{22}^{nn'} = L^{nn'}. \quad (10)$$

3. Results

We have derived the kinetic equations (5), (8) and (9) for the surface ordering and sublayer ordering. These kinetic equations are solved to obtain the kinetic properties of the ordering process in ternary III–V semiconductor alloys.

3.1. Surface ordering

First, by studying (5) we investigate the surface ordering process without considering the influence of the sublayer. Setting $d\eta/d\tau = 0$ in (5), we obtain the equilibrium solution to the kinetic equation:

$$T = \frac{E_0 + (W_2 - W_1)\eta_e}{k_B \ln[(1 + \eta_e)/(1 - \eta_e)]} \quad (11)$$

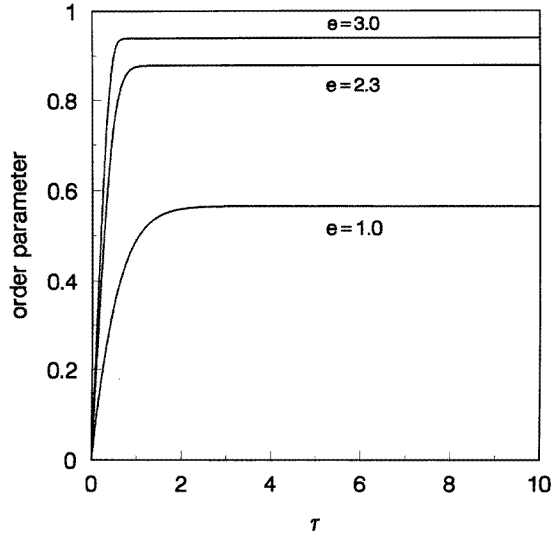


Figure 5. Evolution of the long-range order parameter η as a function of reduced time τ for $a = 0.5$ and three positive values of e : $e = 1.0$, $e = 2.3$ and $e = 3.0$.

where η_e is the equilibrium order parameter. The critical temperature is given by $\eta_e = 0$:

$$\begin{aligned} T_c &\rightarrow \infty & E_0 &\neq 0 \\ T_c &= \frac{W_2 - W_1}{2k_B} & E_0 &= 0. \end{aligned} \quad (12)$$

Therefore, when on-site energy $E_0 \neq 0$ the critical temperature at which $\eta_e = 0$ approaches infinity, that is, in the mean-field approximation there is no phase transition on the reconstructed surface. When $E_0 = 0$, i.e., there is no reconstruction on the surface, we obtain finite T_c from (12). Using the results of interaction energies from the first-principles calculation of the unreconstructed surface in the GaInP alloy [11], we have $T_c \approx 264$ K for the unreconstructed surface. Since this value of critical temperature is much lower than the typical growth temperature (≈ 900 K), the initial disorder can only evolve into a vanishing order parameter at growth temperature. Thus, the unreconstructed case cannot lead to the observed CuPt-type ordering.

Therefore, to study the ordering process of the reconstructed surface, kinetic equation (5) with nonzero E_0 is solved numerically. The initial value of the order parameter is assigned to be 10^{-5} , and the evolution of the order parameter η as a function of the reduced time τ is obtained for different values of parameters e and a .

When the usual growth temperature of 900 K is selected in our calculations, the values of the parameters e and a are related to the on-site energy and the interactions of the alloy, respectively, as shown in formula (6). According to the first-principles calculations for the cation-terminated reconstructed surface of GaInP alloy in [11], $e = 2.3$ and $a = 0.65$ are obtained. It is noted that there are four on-site energies for the cation-terminated case in [11]: two of them correspond to $-E_0$ of our model, and the other two correspond to $+E_0$. Here we use the average of their absolute values to calculate e . When the main mode of the surface reconstruction—dimerization—is considered, we have $W_1 \rightarrow W_1/2$ and a is reduced to 0.5.

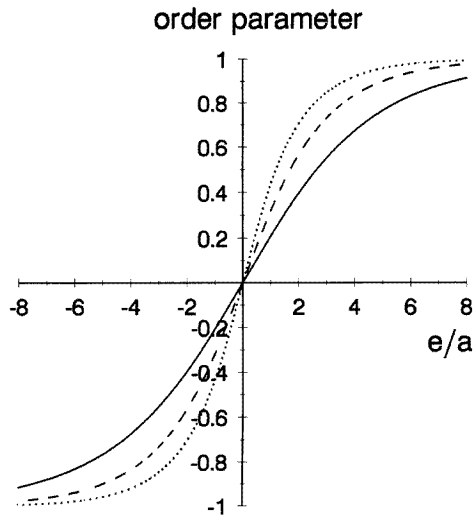


Figure 6. The long-range order parameter $\eta_{\tau \rightarrow \infty}$ evolved for sufficiently long time versus e/a for different constant a : solid curve for $a = 0.35$, dashed curve for $a = 0.5$ and dotted curve for $a = 0.65$.

Figure 5 shows the temporal evolutions of the order parameter for constant $a = 0.5$ and different values of e . With larger absolute value of the on-site energy, the order parameter increases more rapidly and approaches closer to unity. Moreover, it is shown from (5) that the sign of the order parameter η is determined by the sign of the on-site energy E_0 . (We define that $\eta > 0$ corresponds to planar ordered structure O_1 and $\eta < 0$ corresponds to ordered structure O'_1 in figure 3.)

The increase of the order parameter with increasing on-site energy is shown more obviously in figure 6, where the equilibrium order parameter $\eta_{\tau \rightarrow \infty}$ evolved for sufficiently long time versus e/a for different constants a is presented. It is also shown that the curves are symmetric about the zero point, which clearly indicates the influence of the sign of E_0 on the order parameter.

The relation between the long-time order parameter and a/e is shown in figure 7 for different e . $\eta_{\tau \rightarrow \infty}$ increases with the difference between the nearest-neighbour interactions $W_2 - W_1$. In the GaInP alloy $W_1 < 0$ [11], thus the surface dimerization makes $W_2 - W_1$ decrease a little with the change $W_1 \rightarrow W_1/2$. Therefore, as shown in figure 7, the dimerization can slightly decrease the ordering without essential influence.

The growth temperature can also have important effects on the formation of ordered state. As shown in formula (6), the values of e and a increases with decreasing temperature T . Therefore, we can obtain from figures 5–7 that a more highly ordered state will be reached in less time, that is, the ordering process will be accelerated, but the effect is different if the temperature is too low. The surface diffusion rate is greatly reduced at very low temperature, thus, according to formula (6), it takes much longer real time t to reach ordering although it may take less reduced time τ . On the other hand, when the growth temperature is so high that the values of e and a are too small, it will also take much more time to reach a lower degree of order according to figures 5–7. Thus, during the layer-by-layer growth process, it has insufficient time to allow the formation of the ordered structure on the surface before subsequent coverage, so ordering may disappear at too high or too low temperature, which is consistent with the experimental results [1]. Therefore,

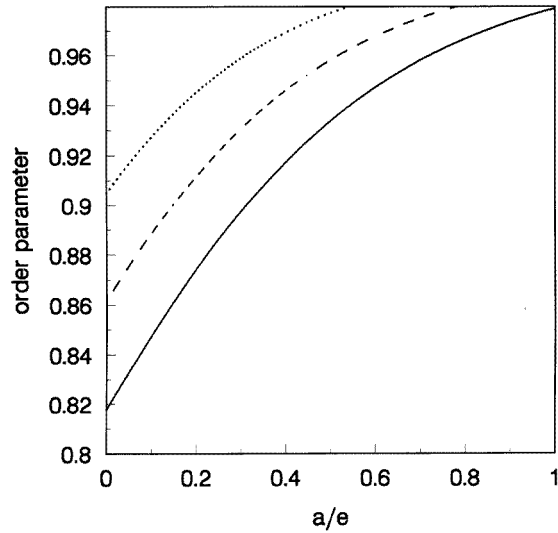


Figure 7. The long-range order parameter $\eta_{\tau \rightarrow \infty}$ evolved for sufficiently long time versus a/e for different constant e : solid curve for $e = 2.3$, dashed curve for $e = 2.6$ and dotted curve for $e = 3.0$.

the growth temperature has important influences on the order–disorder process of epitaxial growth in spite of the results that no phase transition occurs on the reconstructed surface.

3.2. Sublayer ordering and stacking

During the layer-by-layer growth process the influence and interactions between the surface layer and sublayer are to be investigated. Thus, we study the kinetic equations (8) and (9) derived in section 2, and rewrite them as

$$\frac{d\eta_0}{d\tau} = e + a\eta_0 + \ln \frac{1 - \eta_0}{1 + \eta_0} + l_1 \left(e_2 + a_2\eta_2 + \ln \frac{1 - \eta_2}{1 + \eta_2} \right) \quad (13)$$

and

$$\frac{d\eta_2}{d\tau} = l_2 \left(e + a\eta_0 + \ln \frac{1 - \eta_0}{1 + \eta_0} \right) + l_3 \left(e_2 + a_2\eta_2 + \ln \frac{1 - \eta_2}{1 + \eta_2} \right) \quad (14)$$

respectively, where the expressions for e , a , and τ are the same as those in (6) for surface ordering except that the diffusion coefficient and the interactions within the surface layer are denoted as L^{00} , W_1^0 , and W_2^0 instead of L , W_1 , and W_2 , and parameters e_2 and a_2 are related to the on-site energy and the interactions of the sublayer, that is,

$$\begin{aligned} e_2 &= E_2/k_B T \\ a_2 &= (W_2^2 - W_1^2)/k_B T. \end{aligned} \quad (15)$$

Parameters l_1 , l_2 , and l_3 in (13) and (14) represent the rates between the sublayer diffusions and the surface diffusion:

$$\begin{aligned} l_1 &= L^{02}/L^{00} \\ l_2 &= L^{20}/L^{00} \\ l_3 &= L^{22}/L^{00} \end{aligned} \quad (16)$$

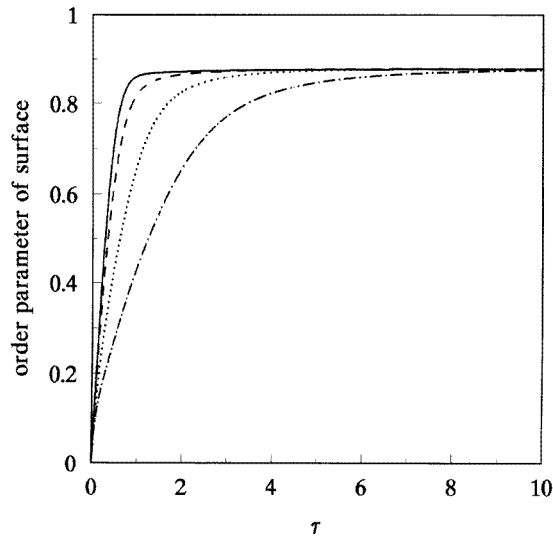


Figure 8. Evolution of the long-range order parameter η_0 of the surface layer as a function of reduced time τ for $l_3/l = 1$ and four different values of l : solid curve for $l = 0.1$, dashed curve for $l = 0.3$, dotted curve for $l = 0.6$, and dot-dashed curve for $l = 0.8$.

and we have $l_1 = l_2 = l$ due to the symmetry of diffusions between layers 0 and 2. Since the sublayer diffusions are much slower than the surface diffusion at typical growth temperature, generally we have $l < 1$ and $l_3 < 1$.

At suitable growth temperature, when the growth rate is low enough that the ordering takes place for sufficient long time on the growing surface before subsequent coverage, the initial value of the sublayer order parameter η_2 after the coverage is taken to be the equilibrium value of the former surface ordering. For example, when we have $e = 2.3$ and $a = 0.5$ for the surface ordering, the surface order parameter evolved for sufficiently long time is 0.88, as shown in figure 5. Thus, we can assign the initial value of η_2 to be 0.88. Initially η_0 is still assigned to be 10^{-5} . Then we solve equations (13) and (14) numerically for different parameters e , a , e_2 , a_2 , l , and l_3 .

First, we fix the parameters $e = 2.3$, $a = 0.5$, $e_2 = 1.3$, and $a_2 = 0.6$ to study the effects of the sublayer diffusions. It is found that if $l_3/l > l$ the equilibrium values of η_0 and η_2 evolved for sufficiently long time are always 0.88 and 0.70, respectively, for any l with $0 < l < 1$, as demonstrated in figures 8–11. In figures 8 and 9, the order parameters of surface layer and sublayer are monitored as functions of reduced time τ for $l_3/l = 1$ and four different values of l , while in figures 10 and 11, l is fixed to be 0.5 and different values of l_3/l are selected. Moreover, it is shown that, although the sublayer equilibrium order parameter decreases slightly from its initial value, the sublayer remains the highly ordered state after evolving for a long time. Therefore, the former ordering surface structure is frozen in, and the sublayer diffusions have no essential influence on the ordering of either surface layer or sublayer.

The effects of l and l_3/l on the ordering process of the surface layer are shown in figures 8 and 10, respectively. Figure 8 demonstrates that it will take less time to reach the equilibrium order for lower l . Thus, low interlayer diffusion between the surface layer and the sublayer can accelerate the surface ordering process. However, low diffusion within the sublayer can slightly delay the ordering process, as shown in figure 10, where, for constant

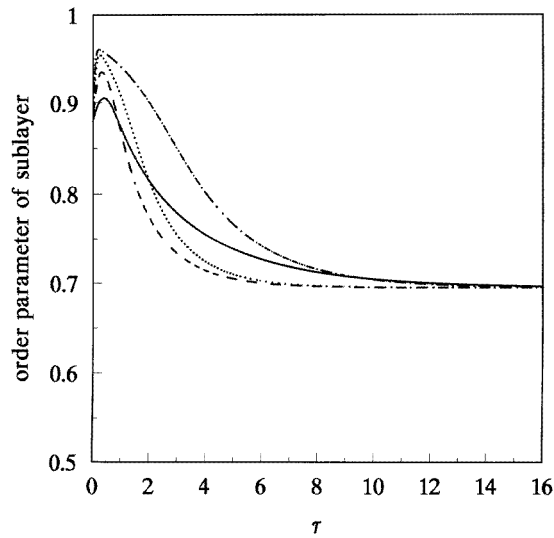


Figure 9. Evolution of the long-range order parameter η_2 of the sublayer as a function of reduced time τ for $l_3/l = 1$ and four different values of l . The notation of the curves is the same as that in figure 8.

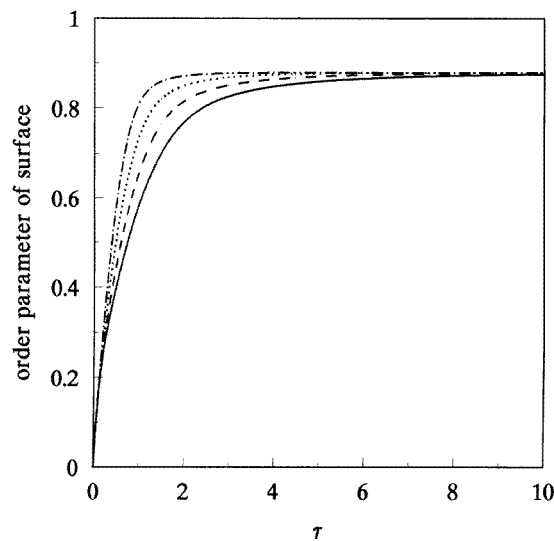


Figure 10. Evolution of the long-range order parameter η_0 of the surface layer as a function of reduced time τ for $l = 0.5$ and four different values of l_3/l : solid curve for $l_3/l = 0.7$, dashed curve for $l_3/l = 0.8$, dotted curve for $l_3/l = 1.0$, and dot-dashed curve for $l_3/l = 1.5$.

$l = 0.5$, the smaller l_3/l is the longer it will take to reach the equilibrium order.

In figures 9 and 11, it is noted that in the early-time regime of the sublayer ordering process the order parameter exhibits a distinct maximum, which is above the long-time equilibrium order of the sublayer. This phenomenon for the sublayer ordering is similar to the overshooting effect reported recently during the ordering process of the kinetic Ising

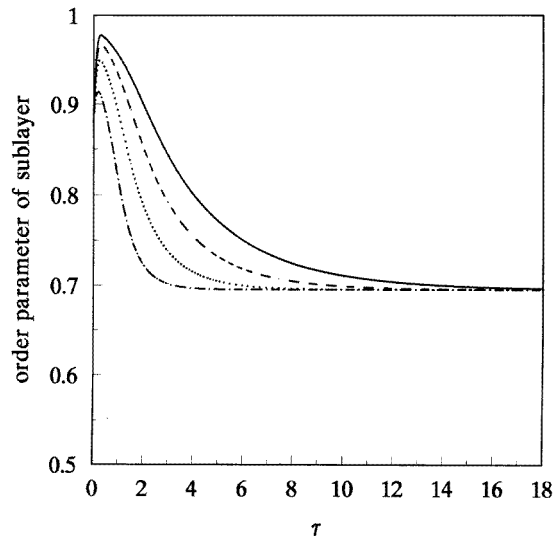


Figure 11. Evolution of the long-range order parameter η_2 of the sublayer as a function of reduced time τ for $l = 0.5$ and four different values of l_3/l . The notation of the curves is the same as that in figure 10.

model [19,20]. Moreover, figures 9 and 11 show that the degree of overshooting increases with increasing interlayer diffusion, which is reflected in l , and decreases with increasing intralayer diffusion within the sublayer, which is reflected in l_3 .

Next, we investigate the influence of parameters e , a , e_2 , and a_2 , which are related to the on-site energies and the interactions of surface layer and sublayer, on the ordering process by fixing l and l_3/l . We find that, similar to the results obtained in section 3.1, the long-time equilibrium order parameter of surface layer (or sublayer) increases with the absolute values of e and a (or e_2 and a_2). However, the changes of e and a (or e_2 and a_2) cannot influence the equilibrium order of sublayer (or surface layer). It is also demonstrated that the sign of the order parameter η_0 or η_2 is determined by the sign of e or e_2 , respectively. Therefore, the signs of the on-site energies E_0 and E_2 determine the selection of the planar ordered structure O_1 or O'_1 for surface layer and sublayer.

Moreover, it is shown from (8) and (9) that the nearest-neighbour interlayer interaction W_{02} does not appear in the kinetic equation, that is, it has no influence on the ordering process. This result is in agreement with the finding of first-principles calculations [11] and phenomenological deductions [17]: there is no effective coupling between the nearest-neighbour layers.

The different layer-by-layer stacking processes of the planar ordered structures O_1 and O'_1 (shown in figure 3) lead to three 3D ordered phases [17, 18]: $1/2L1_1[1\bar{1}1]$ (figure 1(a)) corresponding to the stacking $O_1O_1O_1O_1\dots$, $1/2L1_1[\bar{1}11]$ (figure 1(b)) corresponding to the stacking $O_1O'_1O_1O'_1\dots$, and $1/2[1\bar{1}0]$ (not found in the experiment) corresponding to the stacking $O_1O_1O'_1O'_1\dots$. We verify in the following that only the first two stacking forms can possibly exist in the growth.

According to the results shown above and in section 3.1, the appearance of the planar ordered structure O_1 ($\eta > 0$) or O'_1 ($\eta < 0$) is determined by the sign of the on-site energy, which may be positive or negative during the growth. Therefore, in certain growth conditions, there may be two cases in the layer-by-layer stacking process.

(i) When the on-site energy of the surface has opposite sign before and after one stacking due to the effects of local strains, that is, the signs of E_0 and E_2 are opposite, the adjacent layer structure will be $O_1 O'_1$. Therefore, the corresponding stacking configuration is $O_1 O'_1 O_1 O'_1 \dots$, which leads to the ordered structure $1/2L1_1[\bar{1}11]$.

(ii) When the sign of the on-site energy remains the same during the stacking, that is, the effects of strains remain unchangeable during the growth, the adjacent layer structure will be $O_1 O_1$. Therefore, the stacking configuration is $O_1 O_1 O_1 O_1 \dots$, which corresponds to the ordered structure $1/2L1_1[\bar{1}\bar{1}1]$.

The other possible stacking configuration $O_1 O_1 O'_1 O'_1 \dots$ (corresponding to $1/2[\bar{1}\bar{1}0]$ structure) seems unlikely to appear during the growth, because the influence of the stacking on the on-site energies of the surface will remain fixed during the whole growth process since the growth conditions are unchangeable, that is, the on-site energies before and after one stacking should always be of opposite or the same sign during the stacking process, but in the stacking process of configuration $O_1 O_1 O'_1 O'_1 \dots$ this condition is not fulfilled.

3.3. Order–disorder heterostructure

Recently, the growth of a GaInP order–disorder heterostructure on (001) substrate has been reported [7]. In such a heterostructure, the first few atomic layers are completely disordered and the next few layers are highly ordered with only one variant. The experimental observations demonstrate that the order–disorder interface is abrupt with no defect formation.

The results obtained in the last sections can be applied to investigating the appearance of this order–disorder heterostructure. At high growth temperature, the disordered material with certain thickness is first grown because the atoms cannot have sufficient time to form the ordered structure on the surface during the growth, as shown in section 3.1. Then growth is paused for some time to allow the change to lower temperature. When a new layer is deposited, reconstruction occurs in this surface layer 0, that is, $E_0 \neq 0$. Because of the observed abrupt interface with no dislocations or other defects [7], we assume that the interlayer diffusion between the surface layer and the disordered sublayer almost vanishes. The sublayer will retain its former disordered structure because it has been exposed in the growth interruption for sufficiently long time to be stable and no interlayer diffusion exists. Therefore, the second part of (8) shown in section 2 vanishes, and (8) is reduced to the surface kinetic equation (5). According to the discussion in section 3.1, the ordering of the top layer can have sufficient time to occur before subsequent coverage due to the existence of on-site energy E_0 and the lower growth temperature. The subsequent stacking process leading to the CuPt-type ordered structure is the same as that in section 3.2. Therefore, the heterostructure with adjacent completely disordered and highly ordered materials can be obtained by simply changing the temperature during the growth, which has been verified experimentally in [7].

4. Conclusion

We have applied the microscopic diffusion theory to the ordering process of ternary III–V semiconductor alloys. We show that the on-site energy reflecting the effect of the surface reconstruction plays a central role in the ordering of surface layer and the stacking process. The sign of the on-site energy determines the selection of the planar ordered structures and the formation of the three-dimensional CuPt-type ordered phase variant. The growth temperature has important influences on the order–disorder process of epitaxial growth

although there is no phase transition on the reconstructed surface. We demonstrate that the nearest-neighbour interlayer interaction plays a negligible role in the kinetic ordering process, and at suitable growth temperature the surface ordering occurs and is frozen in after subsequent coverage. At early times in the sublayer ordering process, the sublayer order parameter transiently overshoots the value of the equilibrium order. Through layer-by-layer stacking, two observed variants of CuPt-type ordering are obtained. We also show that in the order–disorder heterostructure the ordering takes place above the disordered layer with an abrupt interface due to the effects of growth temperature.

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