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Thermodynamic analysis of anion exchange during heteroepitaxy

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Abstract

A thermodynamic approach is presented to assess the extent of anion exchange reactions during the heteroepitaxy (molecular beam epitaxy) of dissimilar anion III–V compound semiconductor structures. It is shown that the extent of anion exchange can be predicted by the change in the Gibbs free energy. Bond strength changes can only be used as a guide in comparing the relative tendency for exchange, rather than as a criterion. The driving force for anion exchange strongly depends on the conditions during interface formation. A number of important factors, including bond strength, misfit strain energy, surface structure and energy, the equilibrium between dimers V_2 and tetramers V_4, and segregation are discussed in terms of their contributions to the thermodynamics.

Keywords: A1. Interfacial intermixing; A1. Surface processes; A1. Thermodynamics of anion exchange; A3. Metalorganic vapor phase epitaxy; A3. Molecular beam epitaxy; B2. Semiconducting III–V materials

1. Introduction

During the heteroepitaxy of dissimilar anion III–V semiconductor compounds, the phenomenon of anion exchange may occur and degrade heterojunction interface abruptness. Anion exchange can considerably degrade electronic properties and device performance, resulting in rough, non-abrupt, and/or strained interfaces. A typical example is the challenge of growing arsenide-on-antimonide interfaces. Under certain molecular beam epitaxy (MBE) conditions, an arsenide-on-antimonide interface can extend well over 10 monolayers [1–3], leading to lower carrier mobility and concentration, as well as smaller band-offsets [4–6].

Although anion exchange is typically identified as an undesirable phenomenon, it can also be exploited to create desirable materials properties. In a GaInSb/InAs superlattice, InSb-like bonds can be formed at the GaInSb-on-InAs interface by appropriately controlling the anion exchange. This is desirable, because InSb-like bonds at the interface offer superior structural and electronic properties [7–9]. More recently, Kaspi et al.

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reported excellent structural and optical properties in an InAs/GaSb superlattice structure [40], which was grown in such a manner that InSb-like bonds were formed at the GaSb-on-InAs interfaces, while GaSb-like bonds were formed at the InAs-on-GaSb interfaces by As/Sb exchange [41,42]. In the growth of quantum dots exploiting the Stranski–Krastanov (S–K) growth mode, one of the biggest challenges is the control of dot shape and size. We have used P-for-As exchange to modify InAs dot size and vertical alignment [10,11].

Due to engineering and theoretical importance, many studies have been carried out on As/Sb [1, 12–14], As/P [15–17], and As/N [18] exchange, in order to characterize (down to the atomic level) and control the anion exchange phenomenon. The understanding of this phenomenon has been greatly advanced by the work of Wang [2] and Collins [19], and particularly by the recent work of Xie [20] and Kaspi [21], who have used desorption mass spectrometry to probe the process.

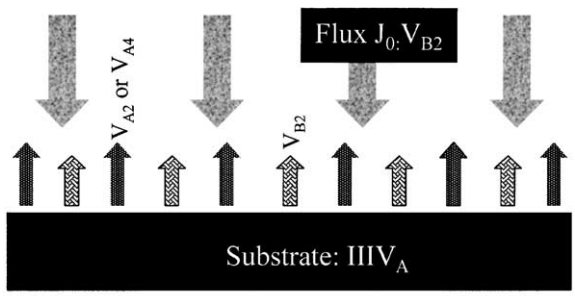
Often, the bond strengths are used to predict whether anion exchange will occur or not. An earlier report showed that weaker-for-stronger-bond exchange (e.g. Sb-for-As, As-for-P, Sb-for-P) cannot occur under typical MBE conditions [22]. However, this was soon proved wrong by Wang [1], who reported that up to 1 ML of As can be replaced by Sb when the As-terminated InAs (0 0 1) surface was exposed to the Sb_2-flux at a temperature of about 380°C. As-for-P exchange was observed experimentally much earlier [15]. A detailed study showed that about two monolayers of InAs are formed on the InP (0 0 1) surface as a result of As-for-P exchange [16]. Further studies showed that As/P exchange can also occur under metal–organic vapor phase epitaxy (MOVPE) conditions [23]. Apparently, the bond strength cannot be generally used as the primary criteria for predicting whether or not anion exchange will occur.

In this paper, we exploit a thermodynamic approach to analyze anion exchange reactions with a focus on the reaction driving force and direction under normal MBE conditions. A number of important factors, including bond strength, misfit strain energy, surface structure and energy, the equilibrium between dimers V_2 and tetramers V_4, and segregation are discussed in terms of their contributions to the thermodynamics.

2. Thermodynamic model

Fig. 1 shows a simplified model of anion exchange under MBE conditions. The surface is exposed to a V_{B2} flux with a beam equivalent pressure (BEP), P_0, or beam flux, J_0, for a unit of time. Then, the V_{B2} beam is shut off and the system is relaxed to equilibrium. After the exchange reaction, V_{B2} molecules depart the surface with a flux, J_{B2}, or BEP, P_{B2}. The exchange product for the group V species may be a mixture of V_{A2} and V_{A4} (e.g. As_2 and As_4), depending on the exchange conditions. For clarity, we first consider V_{A2} only. V_{A4} will be discussed later. The flux and BEP for the product gas V_{A2} are J_{A2} and P_{A2}, respectively. During exchange, the surface is assumed to remain flat, smooth, and coherent to the substrate, although surface roughening occurs in some cases [20,21]. Bulk diffusion is neglected, but in the exchanged layer, diffusion is presumed to be fast enough not to interfere with the exchange process. Assuming no deposition or sublimation, and neglecting the background pressures, mass conservation requires that

$$J_0 - J_{B2} = J_{A2}. \tag{1}$$



Note: the downward arrow represent the inward flux, and the upward ones the desorption flux. The thickness schematically represents the magnitude of the fluxes

Fig. 1. A simplified thermodynamic model of the exchange reaction under MBE conditions. The reaction is represented by: $\mathrm{III}-\mathrm{V_A} + \frac{1}{2}\mathrm{V_{B2}} \leftrightarrow \mathrm{III}-\mathrm{V_B} + \frac{1}{2}\mathrm{V_{A2}}$ (or $\frac{1}{4}\mathrm{V_{A4}}$).

The anion exchange is described as an interfacial reaction

$$\mathrm{III{-}V_A(s)} + \tfrac{1}{2}\mathrm{V_{B2}(g)} \rightarrow \mathrm{III{-}V_B(s)} + \tfrac{1}{2}\mathrm{V_{A2}(g)}. \quad (2)$$

The s and g in brackets stand for solid and gas, respectively. The equilibrium constant, K, for this reaction can be shown to be

$$K = K_{\mathrm{III-V_A}}/K_{\mathrm{III-V_B}}, \quad (3)$$

where $K_{\mathrm{III-VA}}$ and $K_{\mathrm{III-VB}}$ are equilibrium constants for sublimation

$$\mathrm{III{-}V(s)} \leftrightarrow \mathrm{III(g)} + \tfrac{1}{2}\mathrm{V_2(g)}. \quad (4)$$

Listed in Table 1 are the equilibrium constants for the III–V compounds, calculated based on thermodynamic data [24], except those for As_2. As pointed by Hurle [25], the standard heat of formation of As_2 molecules ($\Delta H^0_{298} \sim 53.5$ kcal/mol) was too large. We use the data provided by Pupp [26]. For As_2, the formation heat is 44.4 kcal/mol and 34.4 kcal/mol for As_4. We will use this value in the discussion of the effect of As_4 on the exchange reaction.

The product III–V_B mixes with III–V_A and forms a III–$V_{A(1-x)}V_{Bx}$ solid solution. This process is spontaneous for all the III–V compound semiconductor alloys in the MBE temperature range, although the solution may be metastable (e.g. Ga-$As_{(1-x)}Sb_x$ ternary alloys). Based on a regular solution model [43], the activities of the components in the solution, denoted by [III–V], take the form

$$[\mathrm{III{-}V_A}] = x\exp[W(1-x)^2/kT], \quad (5)$$

$$[\mathrm{III{-}V_B}] = (1-x)\exp[\Omega x^2/kT], \quad (6)$$

where the interaction energy Ω and kT are measured in electron volts (eV).

By definition [43], the reaction quotient Q for the exchange reaction (2) is written as

$$Q = \frac{[\mathrm{III{-}V_A}]}{[\mathrm{III{-}V_B}]}\left(\frac{P_{A2}}{P_{B2}}\right)^{0.5} = \frac{x}{1-x}\exp\left[\frac{\Omega}{kT}(1-2x)\right]\left(\frac{P_{A2}}{P_{B2}}\right)^{0.5}. \quad (7)$$

Let ρ_s represent the atomic density on the surface and N represent the number of monolayers participating in the exchange reaction, the total number, N_t, of V_A atoms being replaced by V_B is

$$N_t = xN\rho_s = xN_s = 2J_{A2}. \quad (8)$$

The partial pressure P_i and the beam flux J are interrelated by [44]

$$J = \alpha\frac{P_i}{\sqrt{m_i T}}, \quad (9)$$

where m_i is the molecular weight and α is a geometrical factor. By combing Eqs. (1), (8) and (9) to get P_{A2}/P_{B2} and plugging it into Eq. (7),

Table 1
Equilibrium constants for sublimation of III–V Compounds and the maximum sublimation temperature (T_{sub1}) and the temperature of non-congruent dissociation (T_{sub2})

Reaction	$K_{III-V} = P_{III}P_V^{1/2}$ (kT in eV)	T_{sub1} (°C)	T_{sub2} (°C)
$Al_{(g)} + 1/2P_{2(g)} \leftrightarrow AlP_{(s)}$	$3.86 \times 10^{11}\exp(-5.84/kT)$		
$Al_{(g)} + 1/2As_{2(g)} \leftrightarrow AlAs_{(s)}$	$5.00 \times 10^{11}\exp(-5.58/kT)$	902	974
$Al_{(g)} + 1/2Sb_{2(g)} \leftrightarrow AlSb_{(s)}$	$2.79 \times 10^{11}\exp(-5.10/kT)$		
$Ga_{(g)} + 1/2P_{2(g)} \leftrightarrow GaP_{(s)}$	$4.19 \times 10^{11}\exp(-4.58/kT)$	571	774
$Ga_{(g)} + 1/2As_{2(g)} \leftrightarrow GaAs_{(s)}$	$5.44 \times 10^{11}\exp(-4.55/kT)$	630	723
$Ga_{(g)} + 1/2Sb_{2(g)} \leftrightarrow GaSb_{(s)}$	$2.71 \times 10^{12}\exp(-4.53/kT)$		
$In_{(g)} + 1/2P_{2(g)} \leftrightarrow InP_{(s)}$	$1.66 \times 10^{11}\exp(-4.14/kT)$	268	684
$In_{(g)} + 1/2As_{2(g)} \leftrightarrow InAs_{(s)}$	$2.05 \times 10^{11}\exp(-4.09/kT)$	508	688
$In_{(g)} + 1/2Sb_{2(g)} \leftrightarrow InSb_{(s)}$	$4.37 \times 10^{10}\exp(-3.97/kT)$		
$Ga_{(g)} + 1/4Sb_{4(g)} \leftrightarrow GaSb_{(s)}$	$2.73 \times 10^{10}\exp(-3.88/kT)$		
$In_{(g)} + 1/4Sb_{4(g)} \leftrightarrow InSb_{(s)}$	$4.39 \times 10^{8}\exp(-3.32/kT)$		
$As_{2(g)} \leftrightarrow 1/2As_{4(s)}$	$5.00 \times 10^{-5}\exp(1.18/kT)$		

we get

$$Q = \frac{x}{1-x}\exp\left[\frac{\Omega}{kT}(1-2x)\right] \times \left(\frac{m_{A2}}{m_{B2}}\right)^{0.2.5}\left(\frac{2J_0}{N_s x}-1\right)^{-0.5}, \quad (10)$$

where m_{A2} and m_{B2} are the molecular weights of V_{A2} and V_{B2}. When the reaction reaches its equilibrium, $Q = K$, and then, the molar fraction of exchange, x, is determined. In this equation, the exponential term measures how far the solid solution deviates from an ideal solution.

The number of monolayers, N, in the exchange reaction is unknown. Considering bulk diffusion can be neglected, it is reasonable to assume $N < 3$, although up to 4.5 monolayers has been recently reported [21]. In our calculation, we use the ratio J_0/N_s as an input. One can readily incorporate the thickness of the exchanged layer into our results. However, for the sake of clarity, our discussion assumes one monolayer exchange and the exposed surface is (0 0 1). In this case, for BEP $= 10^{-6}$ Torr, J_0/N_s is about 0.2 ($\rho_s \sim 5.5 \times 10^{14}\,\mathrm{cm}^2$).

3. Results

Both weak-for-strong-bond and strong-for-weak-bond exchanges have been experimentally identified. In this section, we take P-for-As (strong-for-weak) and Sb-for-As (weak-for-strong) exchanges as examples to illustrate the thermodynamic characteristics of the exchange reactions. As will be shown below, the equilibrium constants for the exchange reactions are weakly temperature dependent. The impact of temperature is much less remarkable than other factors, such as J_0. Therefore, in our examples, we have tried to use the same temperatures as experimentally used, so that one can conveniently make direct comparisons.

3.1. P/As exchange

As discussed in most of experimental research, strong-for-weak-bond exchange is always expected to occur under normal exposure experimental conditions. This is exactly what we obtain from thermodynamic prediction, as shown in Fig. 2(a) and (b), where the exposed surfaces are GaAs (0 0 1) and InAs (0 0 1), respectively. The arrowheads indicate the exchanged molar fraction at equilibrium. The exchange reactions and their equilibrium constants for these two cases are

$$\mathrm{GaAs(s)} + \tfrac{1}{2}\mathrm{P_2(g)} \rightarrow \mathrm{GaP(s)} + \tfrac{1}{2}\mathrm{As_2(g)},$$
$$K = 1.30\exp(0.035/kT),$$

$$\mathrm{InAs(s)} + \tfrac{1}{2}\mathrm{P_2(g)} \rightarrow \mathrm{InP(s)} + \tfrac{1}{2}\mathrm{As_2(g)},$$
$$K = 1.23\exp(0.052/kT).$$

It can be seen that the exchanged molar fraction, x, of GaP or InP increases with the ratio of J_0/N_s. Under small fluxes ($J_0/N_s < \sim 0.25$), almost all the

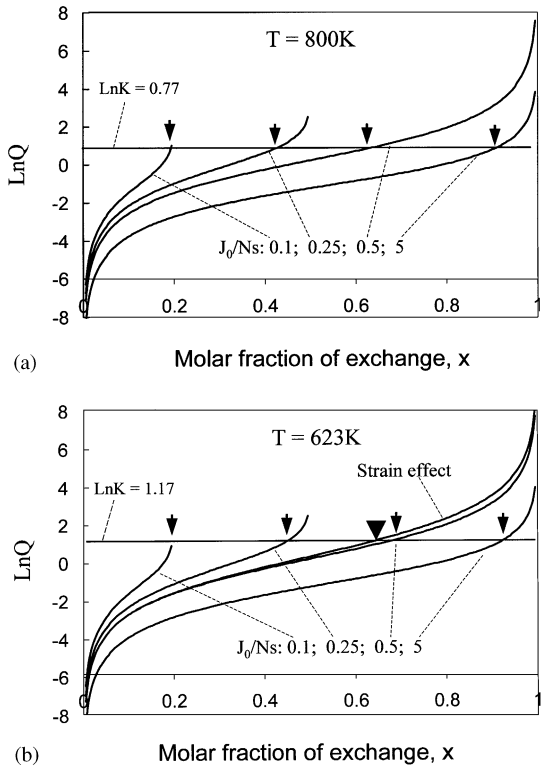


Fig. 2. Variation of the reaction quotient LnQ with molar fraction of exchange x under different exposure flux for the strong-for-weak-bond exchange. LnK is represented by the horizontal line. The arrowheads indicate the amount of exchange at equilibrium. The solid triangle indicates the amount of exchange at equilibrium when the strain effect is considered. (a) GaAs (0 0 1) exposed to P_2; (b) InAs (0 0 1) exposed to P_2.

incoming P_2 molecules are exchanged. When the flux increases to $0.5N_s$, which corresponds to a BEP of about 1.6×10^{-6} Torr (assuming one monolayer exchange), about 60% of the As atoms in an InAs (0 0 1) monolayer are replaced by P atoms. It can also be seen that the degree of exchange increases with the increase in bond strength difference.

It should be noted that the backward reaction represents the As-for-P (weak-for-strong) exchange. Therefore, under the same J_0/N_s condition, the As-for-P exchange can hardly occur for small J_0/N_s. To get appreciable exchange, the J_0/N_s should be larger than $\sim1\times10^{-6}$ Torr.

3.2. Sb/As exchange

Owing to the large challenge in fabricating abrupt and smooth antiminide-on-arsenide interface, Sb/As anion exchange has been studied since late 1980s [39]. The experimental results have shown that the exchange reaction in both directions can occur [1,2,20,21]. Complete exchange of one monolayer was observed for the Sb-for-As case [1], and several monolayers of exchange were observed for As-for-Sb [20,21].

In Fig. 3 the variation of the reaction quotients with molar fraction x of exchange under different J_0/N_s conditions is shown. The exposed surfaces are GaAs (0 0 1) and InAs (0 0 1). The exchange reactions and equilibrium constants are, respectively,

$$\mathrm{GaAs(s)}+\tfrac{1}{2}\mathrm{Sb_2(g)}\rightarrow\mathrm{GaSb(s)}+\tfrac{1}{2}\mathrm{As_2(g)},$$
$$K=0.20\exp(-0.02/kT),$$

$$\mathrm{InAs(s)}+\tfrac{1}{2}\mathrm{Sb_2(g)}\rightarrow\mathrm{InSb(s)}+\tfrac{1}{2}\mathrm{As_2(g)},$$
$$K=4.69\exp(-0.12/kT).$$

As expected, the weak-for-strong-bond exchange is very small. For example, under $J_0/N_s=0.25$, which corresponds to a BEP of 1.6×10^{-6} Torr, $x=0.05$ for GaAs (0 0 1). Most of the Sb_2 molecules are left unchanged. In contrast, almost all As_2 molecules are exchanged for the As-for-Sb reactions under the same conditions, qualitatively in agreement with the experimental observations.

There is a disagreement in the extent of Sb-for-As exchange between the thermodynamic prediction and the experimental values. Under a BEP of approximately 3.0×10^{-6} Torr ($J_0/N_s=\sim0.5$), the molar fraction, x, of InSb exchanged is about 0.3, much smaller than the experimental observations (about 1 ML). We tend to think that this disagreement may be attributed to the involvement of As_4 in the exchange reaction. This will be discussed in detail in the following section.

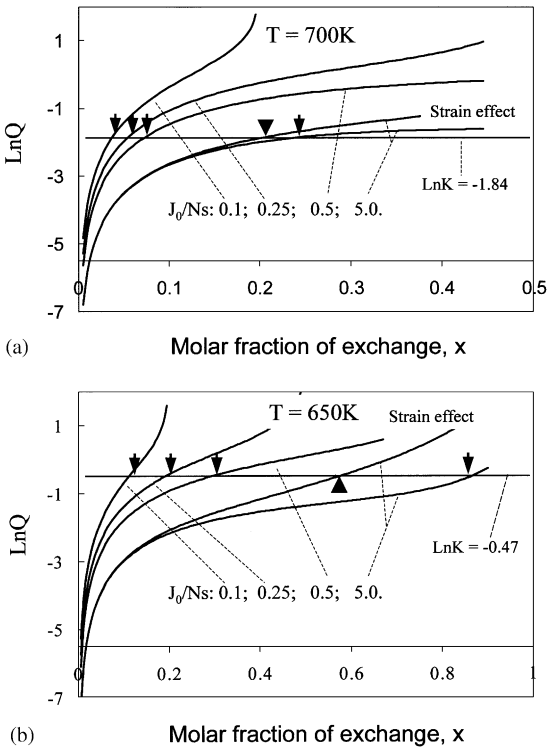


Fig. 3. Variation of the reaction quotient LnQ with molar fraction of exchange x under different exposure flux for the strong-for-weak-bond exchange. LnK is represented by the horizontal line. The arrowheads indicate the amount of exchange at equilibrium. The solid triangle indicates the amount of exchange at equilibrium when the strain effect is considered. (a) GaAs (0 0 1) exposed to Sb_2; (b) InAs (0 0 1) exposed to Sb_2.

The above two examples demonstrate that both the weak-for-strong and strong-for-weak exchange reactions will occur under typical MBE soaking conditions. Bond strengths, which will be discussed in detail later, cannot be used as criteria for the occurrence of the anion exchange reaction. However, higher bond strengths do indicate a larger tendency of the exchange reaction. These

observations can generally be extended into other materials systems, including binary, ternary, etc. semiconductor alloy systems. For example, the As-for-P exchange reaction may occur in the As-soaking of InP (0 0 1) surface, or even during the initial growth of the GaInAs on InP in the GaInAs/InP systems. Since the As-for-P is a weak-for-strong exchange, the amount of exchange is relatively small. For example, InAs (0 0 1) exposed to a P_2 flux of $0.5N_s$ at 800 K results in about 0.68 ML P-for-As exchange, while InP (0 0 1) surface exposed to As_2 under the same conditions gives rise to about 0.23 ML P-forAs exchange (see Fig. 2b). In the GaAsSb-on-InP systems, both As-for-P and Sb-for-P exchange reactions may happen simultaneously during the growth of GaAsSb. However, the degree of As-for-P exchange may be larger due to the higher In–As bond strength than In–Sb. The actual amount of exchange needs to consider other factors, as discussed below.

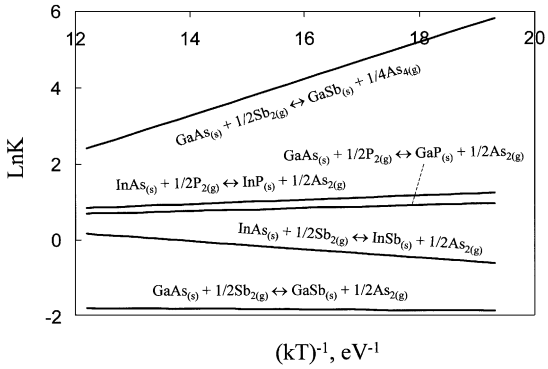


Fig. 4. Temperature dependence of equilibrium constant for some typical exchange reactions.

4. Discussion

It can be seen from the above thermodynamic analysis that anion exchange of either strong-for-weak-bond or vice versa can both occur, depending on the experimental conditions and material properties. These predictions qualitatively agree with the experimental observations. However, in reality, there are a number of factors that may have large impact on the thermodynamic equilibrium. They may not be able to reverse the reaction directions, but they are indeed able to shift the equilibrium point. These factors are discussed in detail below.

4.1. Bond strength

Although the exchange reaction is often discussed in terms of bond strength, the direction of exchange reaction is determined by the total free energy change, rather than by the bond strength. However, under normal MBE conditions, the bond strength can be used as a first guide for determining the tendency of exchange. Fig. 4 shows the equilibrium constants in the MBE temperature range for some typical exchange reactions. Note the weak temperature dependence of the equilibrium constants. It can be seen that the larger differences in bond strength have larger equilibrium constants for strong-for-weak-bond exchange (or smaller K for weak-for-strong-bond exchange), implying larger degree of exchange.

4.2. Mixing interaction energy

When foreign or solute atoms are put into a host lattice, lattice distortion is produced corresponding to the atomic size difference. The amount of strain energy, related to the lattice distortion, and also the chemical potential of the constituent components, is measured in terms of the mixing interaction energy. The effect of the interaction on the equilibrium of the exchange reaction is reflected by the term $\exp[(1-2x)\Omega/kT)]$. The interaction energy Ω, related to the regular solution model, has been shown to be directly proportional to the square of lattice mismatch. Based on the delta-lattice-parameter model, proposed by Stringfellow [27], the interaction energy Ω is 147.5 meV for Ga–As–Sb, 98.5 meV for In–As–Sb, 42.5 meV for Ga–As–P, and 25.2 meV for the In–As–P system. Consequently, the greatest effect of the interaction energy is expected in the Ga–As–Sb ternary alloys. The equilibrium point is shifted in the lower x direction when $x<0.5$ (usually for weak-for-strong-bond exchange), and

for $x > 0.5$, to the higher x direction. Interpretation for this effect is simple. When $x < 0.5$, the lattice distortion energy increases with addition of solute V_B atoms to the host III–V_A lattice. This energy increase process automatically results in shifting of the equilibrium point to smaller x. For $x > 0.5$, the host lattice is converted from III–V_A to III–V_B. Increasing x is equivalent to decreasing the solute (now V_A) concentration, and hence the equilibrium is shifted to higher x values. A quantitative comparison is shown in Fig. 5. It can be seen that remarkable effects can be expected when the equilibrium x is away from 0.5.

4.3. Strain energy

As a result of atomic differences, the lattice constant of the solid solution III–$V_{A(1-x)}V_{Bx}$ is different from that of the substrate III–V_A, giving rise to a lattice mismatch between them. Consequently, the surface layer is strained and elastic strain energy is built up during the anion exchange, thereby increasing the chemical potential of the constituent components. The amount of strain energy stored depends on the molar fraction x. Using the basic elastic theory [45], and assuming the lattice constants obey the Vegard's law and no plastic relaxation occurs, the strain energy E_{str} (in eV) can be found to take the form of

$$E_{str} = 1.037 \times 10^{-11} \frac{m_i}{\rho}\left(C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}}\right)\varepsilon_0^2 x^2, \tag{11}$$

where m_i is the atomic weight, ρ the density (g/cm^3); the C's are elastic constants (Pa), ε_0 the misfit strain when $x = 1$.

As expected, the stored strain energy in the exchanged surface layer always shifts the equilibrium point to lower molar fractions. In other words, the strain effect always resists the exchange process on a strain-free flat surface. This is in contrast with the case where anion exchange is used to modify dot morphology. In this case, the strain energy in the system maybe reduced by the anion exchange, thereby providing a driving force for the shrinkage of the dots in size.

The lattice mismatch hardly causes any change in the crystallinity, so the corresponding change in entropy is about zero, e.g. $\Delta S \approx 0$. Therefore, the lattice mismatch causes an additional change in the Gibbs free energy:

$$\Delta G_{str} = \Delta H_{str} - T\,\Delta S_{str} \approx \Delta H = E_{str}. \tag{12}$$

It can now be shown that the equilibrium constant K is reduced by a factor of $\exp(E_{str}/kT)$. So the effective equilibrium constant

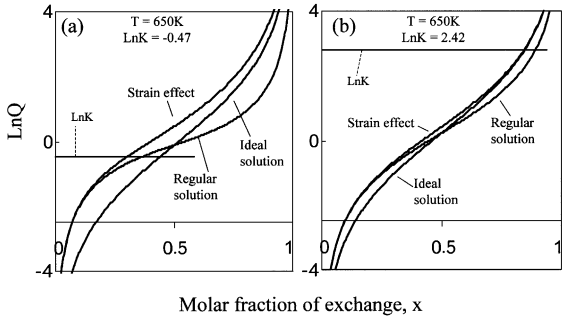


Fig. 5. Variation of the reaction quotient LnQ with molar fraction of exchange x to show the effect of interaction energy (regular solution) and strain energy on molar fraction of exchange at equilibrium with respect to the ideal solution (interaction energy = 0, and strain energy = 0). The intersection beween LnQ and LnK represents the amount of exchange at equilibrium. (a) InAs (0 0 1) exposed to Sb_2; (b) GaAs (0 0 1) exposed to P_2.

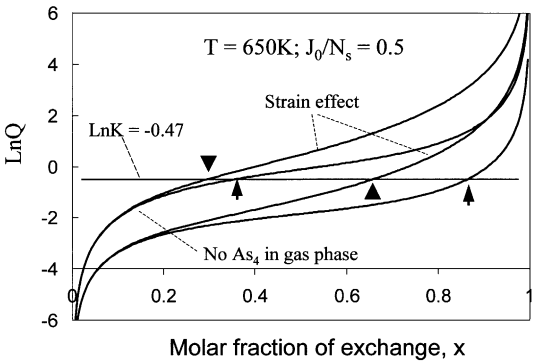


Fig. 6. Variation of the reaction quotient LnQ with molar fraction of exchange x to show the effect of the equilibrium between As_2 and As_4 on the exchange reaction. The arrowheads indicate the amount of exchange at equilibrium. The solid triangle indicates the amount of exchange at equilibrium when the strain effect is considered. InAs (0 0 1) exposed to Sb_2.

becomes

$$K_{\text{eff}} = \exp[-(\Delta G + \Delta G_{\text{str}})/kT] = K\exp(-E_{\text{str}}/kT). \quad (13)$$

The effect of strain energy on the equilibrium is shown in Fig. 5, where the contributions of non-ideality of the solid solution and strain effect are compared with respect to the ideal solution. More comparisons are shown in Figs. 2, 3 and 6.

4.4. V_4 effect

For group V species, an equilibrium exists between tetrameric and dimeric form:

$$V_2(g) \leftrightarrow \tfrac{1}{2}V_4(g), \quad K_{V4} = P_{V4}^{1/2}P_{V2}^{-1}. \quad (14)$$

Depending on the exchange temperature, this equilibrium can have drastic impact on the exchange reaction. It is reported that, within the temperature range of 530–730°C, P_2 is the dominant phosphorus species over InP. Only up to 10% of the total phosphorus flux consists of P tetramers [28,29]. Fluxes originating from the (0 0 1) InP surface heated in the UHV between 330°C and 420°C consist of only P dimers [28]. These results indicate that in the practical exchange temperatures, the involvement of P tetramers can be neglected.

For $Sb_2(g) \leftrightarrow 1/2Sb_4(g)$, it is predicted that the equilibrium antimony species is the Sb tetramer dominant below 530°C, based on the thermodynamic data [30]. Under a total pressure in the range of 10^{-7}–5×10^{-6} Torr, about 90% of the molecules are Sb_4. Therefore, Sb_4 molecules are expected to dominate in the flux from the surface at typical MBE conditions. Some earlier preliminary experimental results [31,32] support this prediction. However, Sb_4 is not mentioned in the recent reports [20,21].

For $As_2(g) \leftrightarrow 1/2As_4(g)$, experimental results indicate that below 350°C, the tetameric As_4 dominates in the flux from a heated GaAs surface, irrespective of the type of arsenic molecules impinging on the surface. At temperatures of 450°C and higher, dimeric arsenic molecules take over in dominance [33,34]. These results essentially agree with the thermodynamic predictions [35,36].

When V_4 tetramers are considered, the mass conservation becomes

$$2(J_0 - J_{V2}) = 2(J_{V2} + 4J_{V4}) = xN_s. \quad (15)$$

By coupling reactions (2) and (14) and combining Eqs. (9) and (15), the reaction quotient becomes

$$Q = \frac{x}{1-x}\exp\left[\frac{\Omega}{kT}(1-2x)\right]\left(\frac{4m_{A2}}{m_{B2}}\right)^{0.2.5} \times \left(\frac{\sqrt{1+AN_sx}-1}{A(2J_0 - xN_s}\right)^{0.5}, \quad (16)$$

where A is defined as

$$A = \frac{4K_{V4}^2}{\sqrt{2}}\frac{P_0}{J_0}\left(\frac{m_{A2}}{m_{B2}}\right)^{0.5}.$$

Fig. 6 shows the effect of As_4 involvement in the exchange reaction when InAs is exposed to Sb_2. For convenience of comparison, the no-As_4-involement data is also duplicated form Fig. 3a. It can be seen that the effect of As_4 on the equilibrium is remarkable. The molar fraction x increases from 0.30 to 0.66 under the same exposing conditions. This value is much closer to the experimental observations. This, to some degree, reconciles the disagreement mentioned earlier. From Fig. 4, it can also been seen that the equilibrium constant is very strongly temperature dependent.

4.5. Surface structure and surface energy

Of all the factors influencing the reaction both thermodynamics and kinetics, surface structure and surface energy may be of top importance. Semiconductors have reconstructed surface structures in order to assume a lower energy state under MBE conditions. Therefore, the surfaces may have considerably different thermodynamic properties from their bulk state. As a result, the equilibrium state that is predicted based on the bulk material properties may be far away from the actual one. Unfortunately, few thermodynamic data are available for any quantitative discussion. Intuitively, the shifting of the equilibrium point is expected to be more significant for the case where anion

exchange results in a transition in surface reconstruction (e.g. (1×3) GaSb to (2×4) GaAs) than the case where no surface structure transition is involved.

Anion exchange mostly occurs in the first one or two monolayers. Therefore, the surface energy occupies a large portion in the total energy involved in the exchange process. Even a small change in the surface energy may give rise to a large shift in the equilibrium state. However, due to the lack of surface energy data, we can only make some qualitative assertions. Take the As-terminated (0 0 1) surface energy as a yardstick. It is reported that the surface energy is 2100 meV/nm^2 [37]. So for each As atom, surface energy is about 335 meV, up to ten times higher than the misfit strain energy. For weak-for-strong-bond exchange (e.g. Sb-for-As), the surface energy will be reduced because of the formation of weak bonds on the surface, and hence, the exchange reaction will be favored energetically. In contrast, strong-for-weak-bond exchange will tend to increase the surface energy, and hence will be reduced by the change of surface energy.

4.6. Segregation

In our model, the exchanged molecules are presumed to depart the surface after their exchange. This is not always true. Segregation can occur in some material systems. Although this is a post-exchange process, it can have large impact on the equilibrium point. The most problematic anion is antimony (Sb). It has been reported that, in the heteroepitaxy of InAs/GaInSb structures, the InAs-on-GaInSb interfaces are tens of monolayers thick. The presence of Sb on the growing surface can be detected even at an InAs layer thickness of 200 nm [38]. Much more convincing results are reported recently by Kaspi [21], who used desorption mass spectrometry to monitor the chemistry of the flux departing the surface in situ. The segregated Sb is incorporated into the lattice of the InAs, forming a broad, strained and Sb-graded interface.

Although we can infer from the Sb-segregation phenomenon that the surface energy must be lowered, and hence, the segregation positively influences the anion exchange, we cannot draw any quantitative thermodynamic conclusions. This is because we presently know little about the nature of this segregated layer, including its thickness, the form of the Sb-molecules, etc.

5. Conclusions

The thermodynamic characteristics of the anion exchange reaction in the heteroepitaxy of dissimilar anion III–V compound semiconductor systems have been analyzed under normal MBE conditions. It can be concluded that the driving force for this reaction is the free energy change. The direction of the reaction, e.g., strong-for-weak-bond exchange or weak-for-strong-bond exchange strongly depends on the exposing flux. The bond strength can only be used as a guide for the relative tendency of the exchange, rather than as a criterion. The equilibrium point of the exchange reaction can be greatly shifted by factors such as non-ideality of the solid solution, the misfit strain energy, surface segregation, surface structure and surface energy. The effect of the equilibrium between dimer and tetramer is also discussed.

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