Effect of mixing enthalpy on relaxed and strained growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}_{1-y}$ compound alloys using molecular-beam epitaxy

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The strict virtual crystal model has been shown to describe accurately the mixing enthalpy of III-V ternary alloys. We allocate the different components of this model to both subreactions, i.e., the reactions forming III-V^{I} and III-V^{II} , present in the molecular-beam epitaxial growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}$ compound alloys, and derive thereof a model that describes accurately the composition obtained. A good correspondence with experimental growth data is obtained. We apply this model to both relaxed and strained layer growth and the evolution in the composition is given when a relaxed layer is grown on a substrate with a different lattice constant. © 2000 American Institute of Physics. [S0021-8979(00)01901-0]

I. INTRODUCTION

$\text{III-V}^{\text{I}}\text{V}^{\text{II}}$ compound alloys grown by molecular-beam epitaxy (MBE) are the subject of growing interest due to ongoing research in infrared detectors,¹ infrared light-emitting diodes,² and infrared lasers.³ However, in order to grow these devices accurately, a good knowledge of the MBE growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}$ compound alloys is required.

For better understanding of the MBE growth and all kinetic processes governing the surface morphology, several models were employed including thermodynamic models, *ab initio* calculations, atomistic models using Monte Carlo methods and models based on kinetic rate equations.⁴ Since the MBE-growth process occurs far from thermodynamic equilibrium, thermodynamic approaches seem to be unsuited. However, the Gibbs free energy can be used as a parameter to describe the kinetics of the reaction during the MBE growth.⁴ In this article, we use a thermodynamic model, combined with results from calculations using atomistic models, to describe the MBE growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}_{1-y}$ compound alloys. MBE-grown $\text{III}^{\text{I}}_{1-x}\text{III}^{\text{II}}_{1-x}\text{-V}$ compounds are well studied. The element III composition ratio $x/(1-x)$ is usually direct proportional to the element III flux ratio. This is not the case any more for the MBE growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}_{1-y}$ compound alloys. We discuss in this article the MBE growth of $\text{III-V}^{\text{I}}\text{V}^{\text{II}}_{1-y}$ compound alloys on (111)- and (001)-oriented substrates. In the first section, we calculate the composition ratio $y/(1-y)$ for lattice-matched and relaxed growth under different growth conditions. In the second section, we discuss the strained layer growth. In the next sec-

tion, we describe tentatively the evolution in composition (from the interface) obtained during the MBE growth, if a layer is grown nonlattice matched on a host substrate. This effect is important because composition calibrations are usually done in bulk layers and extrapolated for thin layers. Finally, we draw some conclusions.

II. RELAXED AND LATTICE-MATCHED GROWTH

The case of lattice-matched growth to a substrate or relaxed growth of a layer is considered in this section. Under relaxed growth of a layer with a different lattice constant than the substrate, we understand the growth of a thick layer free from all global strain due to a transition layer where the generation of dislocations accommodated the present strain. Both relaxed layers and lattice-matched layers contain no global strain, only local strain due to the distribution of atoms of different size. In the next sections, we discuss the strained layers and the transition layers between the interface and the relaxed layers.

The MBE growth of III-V compounds ($\text{CA}_y\text{B}_{1-y}$), with C being a type-III atom and A and B being type-V atoms, consists of the mixing of two reactions at the growth surface, i.e., the reactions

$$\text{with } \Delta G_{AC} = \Delta G_{AC0} + RT[\ln(P_A) + \ln(P_C) - \ln(\alpha_{AC})], \quad (1)$$

$$\text{with } \Delta G_{BC} = \Delta G_{BC0} + RT[\ln(P_B) + \ln(P_C) - \ln(\alpha_{BC})]. \quad (2)$$

In the case all atoms are incorporated independently on the surface, this can be rewritten as

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TABLE I. Mixing enthalpy coefficients (Ω/RT) for MBE growth at 450 °C. The values are calculated with data taken from Ref. 6

Compound	Mixing enthalpy coefficient at 450 °C
GaAlAs, GaAlSb	0.00
InAlSb	-1.03
GaInSb	-1.23
InAsSb	-1.55
GaInAs, AlInAs	-1.64
GaAsSb	-1.96
AlAsSb	-2.35

$$A(s) \rightleftharpoons A(g) \quad \text{with} \quad \Delta G_A = \Delta G_{A0} + RT[\ln(P_A) - \ln(\alpha_A)], \quad (3)$$

$$B(s) \rightleftharpoons B(g) \quad \text{with} \quad \Delta G_B = \Delta G_{B0} + RT[\ln(P_B) - \ln(\alpha_B)], \quad (4)$$

$$C(s) \rightleftharpoons C(g) \quad \text{with} \quad \Delta G_C = \Delta G_{C0} + RT[\ln(P_C) - \ln(\alpha_C)], \quad (5)$$

where ΔG_i is the Gibbs free energy for each of the subreactions i and α_i are the activities of the compound i in the solid, as is defined in Ref. 5. The pressures P_i in Eq. (1)–(5) are the macroscopic variables representing the number of molecules per unit of time that impinge on the surface, and are as such equivalent and proportional to atomistic or molecular-beam equivalent pressures (BEP) or fluxes ϕ_i used in MBE. The sum of the BEPs of component A and B is substantially larger than the flux of component C , as is common practice in the MBE growth of III–V compounds and the flux of element C determines the growth rate. Under these conditions, Eqs. (3)–(5) apply rather than Eqs. (1) and (2).

The Gibbs free energy of the combined reaction ΔG equals

$$\Delta G = y\Delta G_{AC} + (1-y)\Delta G_{BC} + \Omega y(1-y) \quad (6)$$

or

$$\Delta G = y\Delta G_A + (1-y)\Delta G_B + \Delta G_C + \Omega y(1-y) \quad (7)$$

with Ω being the mixing enthalpy parameter.⁶

One observes in Table I that the calculated mixing enthalpy coefficient (Ω/RT) is almost equal to zero for compounds as AlGaAs and AlGaSb but that this coefficient is relatively large for InAsSb, AlAsSb, GaAsSb, GaInAs, and InAlAs. We do not further investigate the growth of $\text{III}_x\text{III}_{1-x}\text{V}$ compounds in this article but concentrate on the influence of the mixing enthalpy on III–V_yV_{1-y} compounds.

The calculated mixing enthalpies coefficients in Table I are also experimentally confirmed for a mixture obtained from the liquid.⁷ This coefficient should not be different for a mixture obtained from the gas phase, because most authors link the origin of mixing enthalpy with phenomena taking place in the solid.⁶ The theoretical derivation given below, including this mixing enthalpy is therefore important for the growth of these compounds. The effect of the mixing enthalpy has also been introduced recently for the growth of III–V compounds by metalorganic chemical vapor deposition (MOCVD).⁸

FIG. 1. Tetrahedron cells in a ternary III–V alloy semiconductor (from Ref. 18).

Fedders and Muller⁹ allocated mixing enthalpy to strain energy ΔE_m , which consists of five contributions ϵ_i . Each C atom in the grown layer forms the center of a tetrahedral cell with four atoms at the corners, as shown in Fig. 1. These corner atoms can be either A or B . The type of this cell is determined by the number of B atoms. Each tetrahedral cell¹⁰ has strain energy being (depending on the lattice constant of the host substrate)

$$\begin{aligned} \epsilon_0(z) &= C_B(1-z)^2, & \epsilon_1(z) &= C_B\left(\frac{3}{4}-z\right)^2 + C_D\frac{3}{16}, \\ \epsilon_2(z) &= C_B\left(\frac{1}{2}-z\right)^2 + C_D\frac{1}{4}, & & \\ \epsilon_3(z) &= C_B\left(\frac{1}{4}-z\right)^2 + C_D\frac{3}{16}, & \epsilon_4(z) &= C_B z^2, \end{aligned} \quad (8)$$

where z is hypothetical composition needed to grow a layer lattice matched to the host substrate. C_B and C_D are the effective breathing-mode force constant and the effective displacive mode force constant, respectively. Equation (8) is obtained from the equations in the Appendix of Ref. 11 and Vegards law.

For the relaxed growth and the lattice-matched growths, we investigate in this section, $z=y$, i.e., the concentration y of the compound ($\text{CA}_y\text{B}_{1-y}$) we investigate. If the A and B atoms are distributed randomly the number of tetrahedral cells, the probability function having i A corner atoms on the j occupied corner atoms of the tetrahedral cell (${}^j q_i$) depends on the composition y as

$${}^j q_i = \frac{j!}{i!(j-i)!} y^{j-i} (1-y)^i. \quad (9)$$

The total mixing enthalpy is the sum of all strain contributions being

$$\Delta H = \sum_{i=0}^4 {}^4 q_i \epsilon_i(y) = 2 \frac{C_B + 3C_D}{4} y(1-y) = 2\Omega y(1-y). \quad (10)$$

The relation $(C_B + 3C_D)/4 = \Omega$ is derived from the equivalence with Eq. (6) or Eq. (7).

We now extract the amount each individual reaction contributes to this strain energy. Hereby, we assume that the contribution of the reaction to the strain in the tetrahedral cell is proportional to the number of A or B atoms the reac-

tion contributes to that cell. This assumption is not always justified, because depending on the growth conditions, the strain energy will contribute differently to both reactions as we will point out later.

$$\Delta H_A = \sum_{i=0}^4 \frac{(4-i)}{4} q_i \epsilon_i(y) = \frac{C_B + 3C_D}{4} y(1-y)(\frac{1}{2}+y) = \Omega y(1-y)(\frac{1}{2}+y), \quad (11)$$

$$\Delta H_B = \sum_{i=0}^4 \frac{i}{4} q_i \epsilon_i(y) = \frac{C_B + 3C_D}{4} y(1-y)(\frac{3}{2}-y) = \Omega y(1-y)(\frac{3}{2}-y). \quad (12)$$

We observe that also both subreactions yield a mixing enthalpy proportional to Ω .

$$\Delta G_{AC*} = \Delta G_{AC} + \Delta H_A/y = \Delta G_{AC} + (\frac{1}{2}+y)(1-y)\Omega, \quad (13)$$

$$\Delta G_{BC*} = \Delta G_{BC} + \Delta H_B/(1-y) = \Delta G_{BC} + y(\frac{3}{2}-y)\Omega, \quad (14)$$

$$\Delta G = y\Delta G_{AC*} + (1-y)\Delta G_{BC*}, \quad (15)$$

$$\Delta G_{AC*} - \Delta G_{BC*} = \Delta G_{AC} - \Delta G_{BC} + (\frac{1}{2}-y)\Omega. \quad (16)$$

The proper way to introduce Eq. (13) in Eq. (1) and to introduce Eq. (14) in Eq. (2) is as a correction on the activities α_{iC} of the individual compounds.

Alternatively, one can consider the tetrahedral cells with one C atom and one corner atom (A or B) missing, and evaluate the energy change when these atoms are incorporated. Basically, this approach assumes that there is no strain energy in the cell as long as there is no C atom, making the AC and BC covalent bonds dominant in the strain energy contribution. Because the C atom is a type-III atom, the C atom determines the reaction rate as is common in the III-V MBE growth.

The distribution of atoms on the triangle, where we construct the tetrahedral cell on, equals 3q_i . The strain energy added after a C atom and an A atom have been incorporated, corresponds to

$$\Delta H_A^+ = \sum_{i=0}^3 {}^3q_i \epsilon_i(y) = \frac{C_B + 3C_D}{4} (1-y)(\frac{1}{2}+y) = \Omega (1-y)(\frac{1}{2}+y) \quad (17)$$

and the strain energy added after a C atom and a B atom have been incorporated, corresponds to

$$\Delta H_B^+ = \sum_{i=0}^3 {}^3q_i \epsilon_{i+1}(y) = \frac{C_B + 3C_D}{4} y(\frac{3}{2}-y) = \Omega y(\frac{3}{2}-y), \quad (18)$$

$$\Delta G_{AC*} = \Delta G_{AC} + \Delta H_A^+ = \Delta G_{AC} + (\frac{1}{2}+y)(1-y)\Omega, \quad (19)$$

$$\Delta G_{BC*} = \Delta G_{BC} + \Delta H_B^+ = \Delta G_{BC} + y(\frac{3}{2}-y)\Omega, \quad (20)$$

$$\Delta G_{AC*} - \Delta G_{BC*} = \Delta G_{AC} - \Delta G_{BC} + (\frac{1}{2}-y)\Omega. \quad (21)$$

FIG. 2. MBE growth on a (001) substrate. A or B atoms are dark and C atoms are bright. The last C atom incorporated is marked with horizontal stripes and the last AA and BB molecule with vertical stripes. (a) Initial stage of a new plane, (b) in-line incorporation, (c) side-by-side incorporation, (d) two-layer incorporation.

This approach leads to the same result as described above [Eq. (16)].

If one keeps in mind that the C atom determines the growth rate, the approach described above describes very well the growth on a (111) substrate. Indeed, each C atom incorporated only needs one A or B atom to complete a tetrahedral cell. Two neighboring uncompleted tetrahedral cells are needed to incorporate an AA or BB molecule, but in each cell, only one atom is incorporated.

The growth on a (001) substrate is however different. The initial stage of a new plane is described as follows: when a C atom is incorporated, two A or two B atoms follow immediately, due to the fact that the sum of the BEP of components A and B is assumed substantially larger than the BEP of component C . This growth process is shown in Fig. 2(a). The strain energy added after a C atom and two A atoms have been incorporated, corresponds to

$$\Delta H_A^{++} = \sum_{i=0}^2 q_i \epsilon_i(y) = \frac{C_B(2-y) + C_D(2+y)}{4} (1-y). \quad (22)$$

The strain energy added after a C atom and two B atoms have been incorporated, corresponds to

$$\Delta H_B^{++} = \sum_{i=0}^2 q_i \epsilon_{i+2}(y) = \frac{C_B(1+y) + C_D(3-y)}{4} y, \quad (23)$$

$$\begin{aligned} \Delta G_{AC^*} - \Delta G_{BC^*} &= \Delta G_{AC} - \Delta G_{BC} + (C_B + C_D) \left(\frac{1}{2} - y\right) \\ &= \Delta G_{AC} - \Delta G_{BC} + \frac{1 + C_D/C_B}{1 + 3C_D/C_B} 4\Omega \left(\frac{1}{2} - y\right) \\ &\cong \Delta G_{AC} - \Delta G_{BC} + 2.4\Omega \left(\frac{1}{2} - y\right). \end{aligned} \quad (24)$$

We observe in Eq. (24) that the direct proportionality of the mixing contribution with Ω is broken. The prefactor depends on C_D/C_B which can vary between 0 and 0.7 is typical around 0.5.¹¹ This yields a mixing energy contribution of about $2.4\Omega(1/2-y)$. The maximum mixing energy contribution could be $4\Omega(1/2-y)$.

After this initial stage, the strain energy contribution, and as a consequence, the mixing enthalpy contribution depends on the position a C atom is incorporated. The position where the C atom is incorporated will also reflect the position where the AA or BB pairs are incorporated and completing the tetrahedral cell or cells. (We assume as indicated above that the sum of AA molecule BEP and BB molecule BEP is far higher than the C atom BEP.) Reference 12 indicates that three incorporation methods are present, i.e., “in line,” “side by side,” and “two layer.”

If a C atom is incorporated along the (110) axis with respect to the present step in the growth surface, an in-line AA or BB molecule incorporation is obtained [see upper left corner of Fig. 2(b)], if the two positions are free. The reaction-enthalpy contribution difference is given by Eq. (24). If both positions are not free, no AA nor BB molecule is incorporated. This case should not be considered for the mixing enthalpy contribution.

However, when a C atom is incorporated along the (1 $\bar{1}$ 0) axis with respect to the present step in the growth

surface, and this new atom has a C neighbor along the (110) direction, an AA or BB molecule can be incorporated side by side. This incorporation completes two tetrahedral cells.

Three A or B atoms of the tetrahedral cell are already present in each of those two tetrahedral cells, so the reaction enthalpy contribution difference for each tetrahedral cell corresponds to what can be observed from Eq. (21). [See also Fig. 2(c).]

If the C atom is incorporated at the edge of a present step in the growth surface at an unoccupied position in the AB plane, a typical two-layer incorporation of the AA or BB molecule takes place. If this incorporation completes a tetrahedral cell, the reaction-enthalpy contribution difference is given by Eq. (24). [See also Fig. 2(d).]

One sees clearly that the difference in reaction enthalpy contribution depends strongly on the ratios between the in-line, side-by-side, and two-layer incorporation. Depending on these ratios and the ratio C_D/C_B , a factor n is defined between 1 and 4. We can rewrite Eqs. (21) and (24) as

$$\Delta G_{AC^*} - \Delta G_{BC^*} = \Delta G_{AC} - \Delta G_{BC} + n \left(\frac{1}{2} - y\right) \Omega. \quad (25)$$

Reference 12 gives the following percentages for the incorporation modes when the sum of AA molecule BEP and BB molecule BEP is far higher than the C atom BEP (what we assume in this paper): In-line: 57%, side-by-side: 30%, and two-layer: 13%. If these values are taken, $n = 1.94$. The real value of n is obviously strongly dependent on the growth conditions.

The combined growth rate (r) is defined as the sum of the growth rates of both compounds r_1 and r_2 .¹³ If one considers both reactions completely independent, apart from the correction on the activities given above, one has individual growth rates depending exponential on the energy gained by the reaction,¹⁴ i.e., $r_i \approx c_i \exp(\Delta G_{i^*}/RT)$. If the reverse reaction (desorption) is of any importance, one could include this reverse reaction in a more elaborated discussion.

Alternatively, one can also introduce composition dependent activities α_{iC} , as has been done in Ref. 8. Both approaches lead to the result

$$r = r_1 + r_2 = yr + (1-y)r, \quad (26)$$

$$\begin{aligned} \frac{r_1}{r_2} &= \frac{y}{1-y} \\ &= \frac{C_{AC} \exp(\Delta G_{AC}/RT) \Phi_A}{C_{BC} \exp(\Delta G_{BC}/RT) \Phi_B} \\ &= K \exp\left(\frac{\Delta G_{AC0} - \Delta G_{BC0}}{RT}\right) \frac{\Phi_A}{\Phi_B} \exp[n \left(\frac{1}{2} - y\right) (\Omega/RT)] \\ &= K_0 \frac{\Phi_A}{\Phi_B} \exp[n \left(\frac{1}{2} - y\right) (\Omega/RT)]. \end{aligned} \quad (27)$$

In Ref. 8 (for MOCVD), the mixing enthalpy is distributed over both reactions proportional to the concentration of the other compound, which leads to

$$\Delta G_{AC^*} = \Delta G_{AC} + (1-y)^2 \Omega, \quad (28)$$

$$\Delta G_{BC^*} = \Delta G_{BC} + y^2 \Omega, \quad (29)$$

FIG. 3. Composition ratio as a function the modified flux ratio calculated at a temperature of 450 °C on (a) logarithmic scale and (b) on linear scale, calculated using Eq. (27) with n being equal to 1. [e.g., growth on a (111) substrate]. The sequence of the curves marked with the arrow corresponds to the material list of Table I. The strained layer growth of AlAsSb on both AlAs and AlSb is added as the last curve.

FIG. 4. Composition ratio as a function the modified flux ratio calculated at a temperature of 450 °C on (a) logarithmic scale and (b) on linear scale calculated using Eq. (27) with n being equal to 1.7. The sequence of the curves corresponds with the sequence of Fig. 3.

FIG. 5. Composition ratio as a function the modified flux ratio calculated at a temperature of 450 °C on (a) logarithmic scale and (b) on linear scale calculated using Eq. (27) with n being equal to 2. The sequence of the curves corresponds with the sequence of Fig. 3.

$$\Delta G_{AC*} - \Delta G_{BC*} = \Delta G_{AC} - \Delta G_{BC} + 2\left(\frac{1}{2} - y\right)\Omega. \quad (30)$$

This leads to Eq. (27) with n being equal to 2.

The values of the mixing energies are well known for all III–V compounds.⁶ A typical value of Ω/RT at 450 °C is -1.55 for InAsSb and -2.35 for AlAsSb. Figure 3 shows that the mixing enthalpy has no influence for the growth of $\text{Al}_y\text{Ga}_{1-y}\text{As}$ and $\text{Al}_y\text{Ga}_{1-y}\text{Sb}$ but is dominant for all other III–V compounds such as InAsSb and AlAsSb. The data on Fig. 3 have been plotted for n being equal to 1, i.e., a growth on a (111) substrate or hypothetical growth on a (100) substrate where all V atoms are incorporated in-line. One observes that a higher mixing enthalpy or a lower temperature results in a steeper slope around a composition of 50% (i.e., a composition ratio of 1). This figure indicates, however, that

FIG. 6. Indication of the sensitivity of the composition of MBE grown AlAsSb ($n=1.7$, $T=450$ °C) to a small (5%) change in prefactor. This change can be due to a substrate temperature change. This small prefactor change can cause a AlAsSb composition change of 32%.

each composition can be easily and accurately addressed under these growth conditions. Figure 4 shows the same data for n being equal to 1.7, i.e., a growth on a (100) substrate with dominant side-by-side incorporation. One observes an extremely steep slope for AlAsSb around a composition ratio of 1. This makes it hard but still possible to grow these materials. Experimental results for the growth of AlAs_ySb_{1-y} and InAs_ySb_{1-y} show the same results.¹⁵ Figure 5 shows the same data for n being 2, i.e., for an MOVCD growth or for a growth on a (100) substrate where the number of V atoms incorporated in-line or by two-layer incorporation is above average. It is observed that the composition ratio is not a monotone function of the flux ratio any more for compounds with a large mixing entropy. A miscibility gap is obtained for AlAsSb from 22% to 78%. This effect is growth temperature dependent. Curves resemble more to Fig. 3 as the growth temperature is increased and to Fig. 5 as the growth temperature is decreased. This suggests the growth on a higher substrate temperature, if composition control is important.

A very good control of the substrate temperature and the fluxes are very important in order to obtain an accurate composition of AlAsSb grown on a (100) substrate. Figure 6 shows the substrate temperature sensitivity. A substrate temperature modification leads to a change in $K_0 = K \exp[(\Delta G_{AC0} - \Delta G_{BC0})/RT]$, which can be easily changed by 5%. This 5% change in K_0 can result in a 32% change in composition. The same composition change can be obtained by a 5% change in flux ratio.

III. STRAINED LAYER GROWTH

Composition calibration is usually done on samples with thick, relaxed layers. Often, the same experimental conditions are subsequently used to grow a strained MBE layer with the same composition. However, the influence of strain will result in a different composition, as we point out in this section.

If the layer is grown strained on a substrate with a different lattice constant, the mixing enthalpy changes according to different strain contributions. This results in a mixing enthalpy for the (111) growth of

$$\Delta H_A^* = \sum_{i=0}^3 q_i \epsilon_i(y^*) = \Omega y [(1+3y)(\frac{1}{2} - y^*) + 2y^*{}^2], \quad (31)$$

$$\Delta H_B^* = \sum_{i=0}^3 q_i \epsilon_{i+1}(y^*) = \Omega (1-y) [3y(\frac{1}{2} - y^*) + 2y^*{}^2], \quad (32)$$

$$\Delta G_{AC}^* - \Delta G_{BC}^* = \Delta G_{AC0} - \Delta G_{BC0} + \Omega (\frac{1}{2} - y^*). \quad (33)$$

We consider a^* being the lattice constant of the host substrate. y^* is an hypothetical composition that needs to be used to obtain a lattice constant a^* . y^* can be smaller than zero or bigger than 1. However, in order to obtain lattice-matched growth, at least for the first monolayers, the lattice mismatch of the layer has to be lower than the critical lattice mismatch, which is about 14%.¹⁶ If the layer relaxes afterwards due to the moving of dislocations, the composition is

FIG. 7. Obtained AlAs_ySb_{1-y} concentration as a function of the equivalent concentration y^* representing the lattice constant. These results are given for a set of flux ratios. The constant K_0 is taken 0.33. The diagonal points represent the relaxed layers. (a) shows the model with n being equal to 1, (b) shows the model with n being equal to 2. The latter shows a large unstable region for a flux ratio of 3.

not changed in the layers. If the misfit is above the critical lattice mismatch, the growth is relaxed from the first monolayer on.

If the MBE growth is done on a (001)-oriented substrate, a similar deviation can be done resulting in

$$\Delta G_{AC}^* - \Delta G_{BC}^* = \Delta G_{AC0} - \Delta G_{BC0} + n\Omega(\frac{1}{2} - y^*) \quad (34)$$

with n being a number between 4 and 1.

The composition ratio evolves with the growth rates as in the former section leading to the equation

$$\begin{aligned} \frac{r_1}{r_2} &= \frac{y}{1-y} \\ &= \frac{C_{AC} \exp(\Delta G_{AC}/RT)}{C_{BC} \exp(\Delta G_{BC}/RT)} \frac{\alpha_{BC}}{\alpha_{AC}} \frac{\Phi_A}{\Phi_B} \exp\left(n \frac{\Omega}{RT} (\frac{1}{2} - y^*)\right) \\ &= K \exp\left(\frac{\Delta G_{AC} - \Delta G_{BC}}{RT}\right) \frac{\Phi_A}{\Phi_B} \exp\left(n \frac{\Omega}{RT} (\frac{1}{2} - y^*)\right) \\ &= K_0 \frac{\Phi_A}{\Phi_B} \exp\left(n \frac{\Omega}{RT} (\frac{1}{2} - y^*)\right). \end{aligned} \quad (35)$$

It is observed here that the factor between composition ratio and flux ratio is *independent* of the composition. It is determined only by the nature of the compound and the lattice constant of the substrate used.

If the growth is strained on component AC (i.e., $y^* = 1$), this formula is simplified into

$$\frac{y}{1-y} = K_0 \frac{\Phi_A}{\Phi_B} \exp\left(-n \frac{\Omega}{2RT}\right). \quad (36)$$

If the growth is strained on component BC (i.e., $y^*=0$), this formula is simplified into

$$\frac{y}{1-y} = K_0 \frac{\Phi_A}{\Phi_B} \exp\left(n \frac{\Omega}{2RT}\right). \quad (37)$$

Taking into account that Ω is negative, Eq. (36) shows that the strained growth of $A_yB_{1-y}C$ on AC favors the incorporation of A and Eq. (37) shows that the strained growth of $A_yB_{1-y}C$ on BC favors the incorporation of B .

We added on Figs. 3, 4, and 5 both curves generated by Eqs. (36) and (37) for $\text{AlAs}_y\text{Sb}_{1-y}$, i.e., representing the strained growth on AlAs ($y^*=1$) or GaAs (which has almost the same lattice constant) and the strained growth on AlSb ($y^*=0$). The latter is not so far from the strained growth on InAs .

In Fig. 7 we show how the composition depends on the lattice constant of the host substrate. The upper part is for n being equal to 1 and the lower part for n being equal to 2. The points on the diagonal are the equilibrium concentrations. When a not lattice-matched thick layer is grown, the concentration will evolve by the introduction of dislocations towards these equilibrium values on the diagonal (as indicated by the arrows). The next section describes this evolution. On the lower part of the figure, we observe that the curve corresponding to a flux As/Sb ratio of 3 has three intersections with the diagonal. The two outer intersections represent stable concentrations and the middle intersection is an unstable concentration. The border of the instability region is determined by

$$-n \frac{\Omega}{RT} > 4.5. \quad (38)$$

Unstable growth can as a consequence also be obtained for lower values of Ω by growing at lower temperatures. Unstable growth has been observed for the growth of $\text{InAs}_{1-y}\text{Sb}_y$ ($0.2 < y < 0.8$) at low temperatures (370 °C) as if this unstable growth is not present at 410 °C.¹⁷

IV. COMPOSITION EVOLUTION FROM STRAINED LAYER COMPOSITION TO RELAXED LAYER COMPOSITION

If a thick compound layer is grown on a substrate with a different lattice constant, its composition obviously evolves from the initial strained composition at the interface towards the relaxed composition far from the interface.

We investigate in this section how both y and y^* evolve as a function of distance from the interface. We assume that the growth is done at a constant temperature and with a constant flux ratio (Φ_{V1}/Φ_{V2}).

$y^*(x)$ evolves towards $y(x)$ by the introduction of dislocations (x being the distance from the interface). We assume the probability of a dislocation to be introduced in a unit volume proportional to the square of the misfit. This is a first-order approach. A similar derivation can be introduced for any other dislocation probability.

FIG. 8. Evolution of the concentration y ($\text{AlAs}_y\text{Sb}_{1-y}$) as a function of the normalized distance from the interface for the growth on GaAs and on InAs substrates ($n=1$). This concentration is plotted for several flux ratios.

$$P_d = C_d \epsilon^2 = C_d \frac{(a_{AC} - a_{BC})^2}{a^{*2}(x)} [y^*(x) - y(x)]^2. \quad (39)$$

The lattice constant a^* changes by the Burgers vector b per surface for each dislocation introduced.

$$\frac{\partial a^*(x)}{\partial x} = \frac{b C_d (a_{AC} - a_{BC})^2}{a^{*2}(x)} [y^*(x) - y(x)]^2. \quad (40)$$

a^* equals $a_{BC} + y^*(a_{AC} - a_{BC})$ which leads to

$$\begin{aligned} \frac{\partial y^*(x)}{\partial x} &= \frac{b C_d (a_{AC} - a_{BC})}{a^{*2}(x)} [y^*(x) - y(x)]^2 \\ &\cong \frac{b C_d (a_{AC} - a_{BC})}{\bar{a}^2} [y^*(x) - y(x)]^2 \\ &\cong C_d^*(y^*(x) - y(x))^2. \end{aligned} \quad (41)$$

We have approached the lattice constant by the average lattice constant in the prefactor. We introduce a normalized distance from the surface x^* being x/C_d^* , which leads to the normalized equation

$$\frac{\partial y^*(x)}{\partial x^*} = [y^*(x^*) - y(x^*)]^2. \quad (42)$$

Equation (42) combined with Eq. (35) allows determining the expected concentration evolution as a function of the distance from the interface. The lattice constant of the substrates determines the initial condition for y^* and the initial condition for y is determined from y^* by Eq. (35). Figure 8 shows this evolution for $\text{AlAs}_y\text{Sb}_{1-y}$ grown on GaAs and InAs . Experimental data on the dislocation density allows deducing the normalization factor for the distance from the interface and as a consequence also the concentration profile.

V. CONCLUSION

In this article, we discussed the effect of the mixing enthalpy on the composition of III–V^IV^{II} compound alloys grown by MBE on both (111) and (001) substrates. A thermodynamical model, combined with results atomistic models, is used. A model is derived for lattice-matched, relaxed, and strained layer growth. The difference between the above-cited grown conditions is pointed out. This difference is relevant for device design, because composition calibrations are made on thick relaxed layers, and devices, such as far-infrared lasers, make use of very thin, strained layers. The model in this work allows to derive the exact concentrations, as long as the stochastics used remain valid. This implies that the model remains valid up to the moment microclustering appears in the grown layer. Our model also suggests growing III–V^IV^{II} compounds with extremely low III-compound flux in order to obtain a more accurate concentration around the 50% mixing. We verified our model with our experiments on thick relaxed AlSbAs and InSbAs layers. A good correspondence is obtained.

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