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Abstract
Modelling of the non-equilibrium crystallization of In$_x$Ga$_{1-x}$Sb$_y$As$_{1-y}$ alloys is presented. Formation of the alloy lattice matched to the GaSb or InAs substrate from supercooled liquid solutions is considered. Non-equilibrium crystallization is described by the minimum condition of the Helmholtz free energy of the non-equilibrium heterogeneous system. A simple solution model is used for the liquid and solid phases. The differences in the compositions of the GaSb- and InAs-rich alloys crystallized from supercooled solutions on 10 °C and saturated liquid solutions are demonstrated.

1. Introduction

The In$_x$Ga$_{1-x}$Sb$_y$As$_{1-y}$ alloys play an important role in mid-infrared optoelectronics. In spite of considerable progress in molecular beam epitaxy and metalorganic chemical vapour deposition, liquid phase heteroepitaxy (LPHE) of the In$_x$Ga$_{1-x}$Sb$_y$As$_{1-y}$-based device heterostructures continues to be developed [1, 2]. Further progress in LPHE is strongly connected with extension of the composition range of the In$_x$Ga$_{1-x}$Sb$_y$As$_{1-y}$ alloys grown. In view of the complexity of the multicomponent LPHE processes, extension of this range demands significant efforts for the determination of growth conditions.

Any LPHE process consists of two stages. Actually, the heteroepitaxy takes place only in the first or initial stage since an epitaxial layer grows on a substrate or previous epitaxial layer with another composition. This stage is the most important in LPHE because the difference in the solid state compositions leads to a non-equilibrium growth process. Non-equilibrium results in crystallization of an epitaxial layer concurrent with dissolution of a substrate or previous epitaxial layer. The dissolution changes a liquid solution composition near a growing surface. This change causes the formation of an intermediate layer or even can preclude the

epitaxial growth. In order to reduce the intermediate layer, the crystallization rate should be significantly higher than the dissolution rate. The increase of the crystallization rate can be achieved by increasing the supercooling (SC) of a liquid solution.

High quality LPHE layers should be grown lattice-matched to a substrate. This lattice match can be realized either by the thorough choice of the growth conditions or by the lattice pulling effect established for the first time for the $In_xGa_{1-x}P$ LPHE in [3]. Later, this effect was demonstrated for the $Al_xGa_{1-x}Sb_yAs_{1-y}$, $GaSb_xAs_{1-x}$ and $In_xGa_{1-x}As_yP_{1-y}$ alloys [4, 5]. However, as was shown for LPHE of the III–V ternary alloys, the presence of the lattice pulling effect decreases the deviation from equilibrium of the growth process [6]. This diminution should reduce the growth rate since the deviation from equilibrium is a driving force of crystallization. Therefore, the lattice pulling phenomenon is undesirable for the initial stage of LPHE. The optimal situation for this stage is growth conditions providing crystallization of the lattice-matched layer without this effect. The difference in the solid state compositions formed from saturated and supercooled solutions grows with increasing the lattice mismatch of their constituent compounds [7]. The distinction between the largest and smallest lattice parameters of the constituent compounds of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys is the greatest among the alloys grown by LPHE. Therefore, it is believed that the distinction between the compositions of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys formed from the saturated and supercooled liquid solutions should also be significant. The second stage of LPHE is, in fact, a homoepitaxy since the compositions of the alloys formed in both stages differ slightly. Therefore, crystallization at the second stage can be carried out near thermodynamic equilibrium without dissolution.

Successful modelling considerably facilitates a search of LPHE conditions. Commonly, modelling of LPHE of the III–V quaternary alloys is based on the phase diagrams that represent heterogeneous equilibrium between the liquid solutions and alloys [8]. Therefore, in reality, such modelling could describe the second stage of LPHE and is hardly suitable for the initial non-equilibrium stage.

Non-equilibrium nucleation in supercooled melts has been modelled by maximization of the difference between the free energies of the substances in the liquid and solid phases [9, 10]. Such maximization is equivalent to minimization of the free energy of the same non-equilibrium heterogeneous system [7]. Minimization of the total free energy [7] as well as maximization of the difference [9, 10] mentioned above is, in fact, the expansion of the phase diagram description on the non-equilibrium systems. The approach developed in [7] for the ternary systems can be immediately extended to more component systems.

The aim of this study is modelling of non-equilibrium LPHE of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys formed from supercooled liquid solutions.

2. Model

Crystallization of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy lattice matched to a substrate from a supercooled liquid solution is considered. Heteroepitaxial growth begins after contact of the liquid solution with the substrate. The numbers of atoms in the liquid solution before crystallization are N_{In}^l, N_{Ga}^l, N_{Sb}^l, N_{As}^l. Crystallization is the result of a non-equilibrium process. It is assumed that the Helmholtz free energy of the $(In, Ga, Sb, As)^L$–$(In_xGa_{1-x}Sb_yAs_{1-y})^S$ liquid–solid two-phase system after crystallization is minimal. The numbers of the atoms of the liquid and solid phases are equal to $N_{In}^l - n_{In}^s$, $N_{Ga}^l - n_{Ga}^s$, $N_{Sb}^l - n_{Sb}^s$, $N_{As}^l - n_{As}^s$, n_{In}^s, n_{Ga}^s, n_{Sb}^s, n_{As}^s, respectively. The common LPHE conditions $N_{In}^l \gg n_{In}^s$, $N_{Ga}^l \gg n_{Ga}^s$, $N_{Sb}^l \gg n_{Sb}^s$, $N_{As}^l \gg n_{As}^s$ are used in our calculations. The quantities N_{In}^l, N_{Ga}^l, N_{Sb}^l, N_{As}^l are considered as given values and we let $n^s = n_{In}^l + n_{Ga}^l = n_{Sb}^l + n_{As}^l$ be a parameter. Thus, there are only two independent variables n_{In}^s and n_{Sb}^s. Therefore, the minimum condition

of the Helmholtz free energy of the two-phase system is written as

$$\frac{\partial F}{\partial n^{s}_{In}} = 0, \qquad \frac{\partial F}{\partial n^{s}_{Sb}} = 0. \tag{2.1}$$

The minimum condition of the Helmholtz free energy (2.1) in the simple solution model can be rewritten as

$$y\Delta\mu^{0s} - \mu^{0l}_{In} + \mu^{0l}_{Ga} + \mu^{0s}_{InAs} - \mu^{0s}_{GaAs} + \alpha_{In-Ga}(x^{1}_{In} - x^{1}_{Ga}) - (\alpha_{In-Sb} - \alpha_{Ga-Sb})x^{1}_{Sb}$$
$$- (\alpha_{In-As} - \alpha_{Ga-As})x^{1}_{As} + [\alpha_{InSb-GaSb}y + \alpha_{InAs-GaAs}(1-y)](1-2x)$$
$$+ (\alpha_{InSb-InAs} - \alpha_{GaSb-GaAs})y(1-y) + RT\ln\frac{x^{1}_{Ga}x}{x^{1}_{In}(1-x)} = 0, \tag{2.2}$$

$$x\Delta\mu^{0s} - \mu^{0l}_{Sb} + \mu^{0l}_{As} + \mu^{0s}_{GaSb} - \mu^{0s}_{GaAs} - (\alpha_{In-Sb} - \alpha_{In-As})x^{1}_{In} - (\alpha_{Ga-Sb} - \alpha_{Ga-As})x^{1}_{Ga}$$
$$+ \alpha_{Sb-As}(x^{1}_{Sb} - x^{1}_{As}) + (\alpha_{InSb-GaSb} - \alpha_{InAs-GaAs})x(1-x)$$
$$+ [\alpha_{InSb-InAs}x + \alpha_{GaSb-GaAs}(1-x)] + RT\ln\frac{x^{1}_{As}y}{x^{1}_{Sb}(1-y)} = 0, \tag{2.3}$$

where μ^{0l}_{In} and μ^{0s}_{InSb} are the chemical potentials of the liquid In and solid InSb at the standard state, respectively; z_l and w_{In-Ga} are the coordination number and the interaction parameter between the In and Ga atoms in the liquid phase, respectively; z_2 and $w_{InSb-GaSb}$ are the next-nearest coordination number and the interaction parameter between InSb and GaSb in the alloy, respectively; T is the absolute temperature, $\Delta\mu^{0s} = \mu^{0s}_{InSb} + \mu^{0s}_{GaAs} - \mu^{0s}_{InAs} - \mu^{0s}_{GaSb}$, $\alpha_{In-Ga} = z_l N_{Av} w_{In-Ga}$, $\alpha_{InSb-GaSb} = z_l N_{Av} w_{InSb-GaSb}$, N_{Av} is the Avogadro number, and R is the molar gas constant. The value $\Delta\mu^{0s} = \mu^{0s}_{InSb} + \mu^{0s}_{GaAs} - \mu^{0s}_{InAs} - \mu^{0s}_{GaSb}$ was estimated by

$$\Delta\mu^{0s} = \Delta h^{0} - T\Delta s^{0} + \int_{298.15}^{T}\Delta c\,\mathrm{d}T - T\int_{298.15}^{T}\frac{\Delta c}{T}\,\mathrm{d}T$$

where $\Delta h^{0} = h^{0}_{InSb} + h^{0}_{GaAs} - h^{0}_{InAs} - h^{0}_{GaSb}$, $\Delta s^{0} = s^{0}_{InSb} + s^{0}_{GaAs} - s^{0}_{InAs} - s^{0}_{GaSb}$, $\Delta c = c^{P}_{InSb} - c^{P}_{InAs} - c^{P}_{GaSb} + c^{P}_{GaAs}$, h^{0}_{InSb}, s^{0}_{InSb} and c^{P}_{InSb} are the enthalpy, the entropy at STP and the specific heat capacity of InSb at constant pressure, respectively. The composition of the liquid phase is described by the phase diagram of the (In, Ga, Sb, As)^{L}–(In$_{x_0}$Ga$_{1-x_0}$Sb$_{y_0}$As$_{1-y_0}$)^{S} two-phase system at saturation temperature T_0. The phase diagram is also represented as a minimum condition of the Helmholtz free energy of the heterogeneous system. After the use of the Lagrange method of the undetermined multipliers, the equilibrium conditions are given as

$$x^{1}_{In} + x^{1}_{Ga} + x^{1}_{Sb} + x^{1}_{As} - 1 = 0, \tag{2.4}$$

$$\mu^{0s}_{GaAs} - \mu^{0l}_{Ga} - \mu^{0l}_{As} - \Delta\mu^{0s}x_0 y_0 + [\alpha_{InSb-GaSb}(2x_0 - 1) + \alpha_{InSb-InAs}(2y_0 - 1)]x_0 y_0$$
$$+ (\alpha_{InAs-GaAs}x_0 + \alpha_{GaSb-GaAs}y_0)(x_0 + y_0 - 2x_0 y_0) + RT\ln\frac{(1-x_0)(1-y_0)}{x^{1}_{Ga}x^{1}_{As}}$$
$$- (\alpha_{In-Ga} + \alpha_{Ga-Sb})(x^{1}_{In} + x^{1}_{Sb})(1 - 2x^{1}_{Ga}) + 2\alpha_{In-Sb}x^{1}_{In}x^{1}_{Sb}$$
$$- \alpha_{Ga-As}x^{1}_{Ga}(1 - x^{1}_{As}) - \alpha_{Ga-As}x^{1}_{As}(1 - x^{1}_{Ga}) - (\alpha_{In-As} + \alpha_{Sb-As})$$
$$\times (x^{1}_{In} + x^{1}_{Sb})(1 - 2x^{1}_{As}) = 0, \tag{2.5}$$

$$\mu^{0s}_{InAs} - \mu^{0s}_{GaAs} - \mu^{0l}_{In} + \mu^{0l}_{Ga} + \Delta\mu^{0s}y_0 + [\alpha_{InSb-GaSb}y_0 + \alpha_{InAs-GaAs}(1 - y_0)]$$
$$\times (1 - 2x_0) + (\alpha_{InSb-InAs} - \alpha_{GaSb-GaAs})y_0(1 - y_0) + RT_0\ln\frac{x_0 x^{1}_{Ga}}{(1 - x_0)x^{1}_{In}}$$
$$+ \alpha_{In-Ga}(x^{1}_{In} - x^{1}_{Ga}) + (\alpha_{Ga-Sb} - \alpha_{In-Sb})x^{1}_{Sb}$$
$$+ (\alpha_{Ga-As} - \alpha_{In-As})x^{1}_{As} = 0, \tag{2.6}$$

Table 1. The growth conditions and compositions of the alloys.

	x^1_{In}	x^1_{Ga}	x^1_{As}	x_0 ($T_0 = 570\,°C$, SC $= 0\,°C$)	y_0 ($T_0 = 570\,°C$, SC $= 0\,°C$)
$x = 0.22$, $y = 0.82$ ($T = 560\,°C$, SC $= 10\,°C$)	0.452	0.0483	1.27×10^{-3}	0.199	0.866
$x = 0.83$, $y = 0.18$ ($T = 560\,°C$, SC $= 10\,°C$)	0.497	2.4×10^{-3}	2.95×10^{-2}	0.866	0.164

$$\mu^{0s}_{GaSb} - \mu^{0s}_{GaAs} - \mu^{0l}_{Sb} + \mu^{0l}_{As} + \Delta\mu^{0s}x_0 + [\alpha_{InSb-InAs}x_0 + \alpha_{GaSb-GaAs}(1 - x_0)](1 - 2y_0)$$

$$+ (\alpha_{InSb-GaSb} - \alpha_{InAs-GaAs})x_0(1 - x_0) + RT_0 \ln \frac{y_0 x^1_{As}}{(1 - y_0)x^1_{Sb}}$$

$$+ \alpha_{Sb-As}(x^1_{Sb} - x^1_{As}) + (\alpha_{In-As} - \alpha_{In-Sb})x^1_{In}$$

$$+ (\alpha_{Ga-As} - \alpha_{Ga-Sb})x^1_{Ga} = 0, \tag{2.7}$$

where $\mu^{0s}_{GaAs} - \mu^{0l}_{Ga} - \mu^{0l}_{As} = RT \ln(x^{0l}_{As(Ga)}(1 - x^{0l}_{As(Ga)})) + \alpha_{Ga-As}[1 - 2x^{0l}_{As(Ga)} + 2(x^{0l}_{As(Ga)})^2]$.

The values T, T_0, x and y are considered as given values in our model. The values x^1_{In}, x^1_{Ga}, x^1_{Sb}, x^1_{As}, x_0 and y_0 are calculated from the system of equations (2.2) and (2.3) and (2.4)–(2.7).

3. Results and discussion

The LPHE conditions for the alloys lattice matched to the GaSb and InAs substrates with $x_1 = 0.22$, $y_1 = 0.82$ and $x_2 = 0.83$, $y_2 = 0.18$, respectively, were considered. The growth temperature and SC are equal to 560 and 10 °C, respectively. We took the compositions of the alloys and growth temperature from [1, 2]. The interaction parameters between the atoms in the liquid solution and compounds in the alloy were taken from [10–12], respectively. We used the solubilities of As in In and Ga and solubility of Sb in Ga from [13, 14] and the enthalpies, entropies and heat capacities of the compounds from [15]. The results of the calculations are shown in table 1.

As is seen from table 1, the compositions of the alloys crystallized from the same saturated and supercooled liquid solutions are different. The alloys crystallized from the supercooled solutions contain larger numbers of Ga–As bonds. The increase of the GaAs content at the non-equilibrium crystallization is, apparently, caused by its enthalpy of formation that is the largest among the constituent compounds. Therefore, preferable formation of Ga–As bonds reduces the free energy of the heterogeneous system. At the same time, the increase of Ga–As bonds decreases the concentrations of Ga–Sb and In–As bonds in the considered GaSb- and InAs-rich alloys, respectively. Thus, SC leads to a smaller concentration of the basic component in the one-compound enriched $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys. The concentrations of the bonds were estimated by the supposition of a random distribution of the cations and anions in their sublattices.

Both of the described alloys that crystallized from saturated liquid solutions should have a lattice mismatch ($\Delta a/a \approx 3 \times 10^{-3}$) to the GaSb and InAs substrates. The estimated lattice mismatch is 4–6 times more than at the high quality LPHE of the $In_xGa_{1-x}Sb_yAs_{1-y}$

alloys [16]. At the same time, the lattice mismatches ($\Delta a/a \approx 0.9 \times 10^{-4}$, $\Delta a/a \approx 1.25 \times 10^{-3}$) of the GaSb- and InAs-rich alloys [1, 2], respectively, are considerably smaller. Thus, the influence of SC is very important from the lattice match standpoint. The value of SC at LPHE of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys varies over a very wide range and can even reach 120 °C [17]. It is believed that the difference in the parameters of the epitaxial layers grown from the saturated and supercooled liquid solutions will increase with the increase of SC. Therefore, the developed non-equilibrium approach should be especially important for the greatly supercooled liquid solutions. Moreover, this approach can be immediately extended to modelling of the non-equilibrium LPHE of other $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys.

4. Conclusion

Modelling of the non-equilibrium liquid phase heteroepitaxy of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys from the supercooled liquid solutions is presented. Minimization of the total free energy of the heterogeneous system is used to determine the solid state composition. Differences in the compositions of the alloys crystallized from the supercooled and saturated liquid solutions are demonstrated and discussed. Preferential formation of the Ga–As bonds in the alloys formed from the supercooled solutions is found. The influence of supercooling on the lattice mismatch between GaSb, InAs and the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloys grown is demonstrated.

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