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The miscibility gap of $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys

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Abstract

We present the miscibility gap for the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ quaternary alloys in the regular solution model. The miscibility gap is described in terms of the minimum condition for the free energy of the two-phase decomposed alloy. The alloys are considered in the simple solution and quasichemical approximations. Interactions between the nearest and next nearest atoms as well as the oscillation motion of atoms are taken into account. The miscibility gap of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys is calculated at temperatures of 500, 550, 600 and 650 °C. It is shown that the more correct quasichemical approximation indicates a less extended miscibility gap.

1. Introduction

The $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ semiconductor alloys are the basic materials of mid-infrared optoelectronics. In spite of the considerable progress in molecular beam epitaxy and metal–organic chemical vapour deposition, liquid phase heteroepitaxy (LPHE) of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ -based device heterostructures continues to be developed [1–3]. The alloys are formed from supercooled In-rich or Sb-rich melts. The supercooling of In-rich melts is smaller than the supercooling of Sb-rich melts [1, 3]. The small supercooling provides growth conditions near thermodynamic equilibrium. One of the main problems of LPHE near thermodynamic equilibrium is the extended miscibility gap (MG) of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys [4]. Therefore, the modelling of the MG of such alloys is important.

The $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys are $\text{A}_x\text{B}_{1-x}\text{C}_y\text{D}_{1-y}$ -type alloys. The delta lattice parameter (DLP) and regular solution (RS) models developed in [5, 6] have been used for description of the MG of the $\text{A}_x\text{B}_{1-x}\text{C}_y\text{D}_{1-y}$ alloys [7, 8]. However, the internal energy in the DLP and modified DLP models [4, 5] is not a first-order homogeneous function. For that reason, the free energies of the alloy in these approaches are also not first-order homogeneous functions. However, the first-order homogeneity requirement must be fulfilled for any thermodynamic potential [9]. Therefore, use of the DLP and modified DLP models is unjustified in terms

of thermodynamics. The first-order homogeneity problem is absent for the RS model if the free energy is expressed as a function of numbers of the atoms. The simple solution and quasichemical approximations are the most widely used approaches of the RS model. The more complicated quasichemical approximation is better than the simple solution one because it takes into account correlations between atoms in the alloy [10].

The MG boundary can be represented as a total set of two-phase equilibrium mixtures of the alloys [11]. The conventional heterogeneous equilibrium conditions are expressed as equalities between the chemical potentials of components in the phases [11]. In the DLP and RS models, the cation–anion pair was used as a binary component of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys [5, 6, 8, 12, 13]. The sum of the first two partial derivatives of the free energy with respect to the numbers of cations and anions was called the chemical potential of this binary component [5, 6]. However, a one-to-one correspondence between the numbers of cation–anion pairs and the sums of the first partial derivatives is lacking. In this case, the free energy of the $A_xB_{1-x}C_yD_{1-y}$ alloy is a function of any set of cation–anion pairs corresponding to the numbers of the atoms. Thus, the use of cation–anion pairs ignores the procedure [14] determining the sets of components. Therefore, cation–anion pairs cannot be components of the $A_xB_{1-x}C_yD_{1-y}$ alloy.

The aim of the study is a description of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy MG in the RS model. Generally, the equilibrium state of a thermodynamic system corresponds to the minimum of a relevant thermodynamic potential. In our study, the MG will be described in terms of the minimum condition for the Helmholtz free energy of a two-phase system that is a decomposed alloy. In this case, the two-phase system should be considered as a canonical ensemble. The simple solution and quasichemical approximations will be used in our modelling.

2. The InGaSbAs regular solutions

The $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy in the RS model is based on the following assumptions. The crystal lattice of the alloy is undistorted. The internal energy can be expressed as the interaction energies of the nearest and next nearest atoms. The interaction energy of the next nearest atoms depends on the type of the intermediate atom. The oscillation motion of the atoms is determined by bonds between the nearest atoms. The interaction energies, as well as the oscillation motion, are independent of the surroundings. The degrees of freedom not depending on the arrangement and oscillation motion of the atoms are the internal degrees of freedom. All degrees of freedom are considered separable.

The thermodynamic potential is determined by a partition function of the relevant statistical ensemble [15]. The type of a statistical ensemble is defined by its variables [15]. Temperature and numbers of atoms will be used as variables for the description of the alloy. Therefore, the alloy will be considered as a canonical ensemble. The partition function of the canonical ensemble corresponding to the RS model is expressed in terms of the internal, configurational and acoustic partition functions as [16]

$$Q = Q_{\text{Int}} \sum Q_{\text{Conf}} Q_{\text{Ac}}$$

where the summation is taken over all configurations. The partition function of the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy in the RS model is written as

$$Q = \sigma_i^{N_i} \sigma_j^{N_j} \sum_{i,j=1}^2 \prod g \exp\left(-\frac{u_{ij}}{k_B T}\right)^{N_{ij}} q_{ij}^{N_{ij}} \prod_{l,m=1}^2 \exp\left(-\frac{u_{ijl}}{k_B T}\right)^{N_{ijl}} \exp\left(-\frac{u_{jim}}{k_B T}\right)^{N_{jim}} \quad (1)$$

where i and l are indices of the cations, j and m are indices of the anions, σ_i is the internal partition function of the i th-type cation, σ_j is the internal partition function of the j th-type

anion, N_i and N_j are numbers of the i th-type cations and the j th-type anions, respectively, g is the number of geometrically different configurations having the same value of the internal energy, u_{ij} is the energy of interaction between the nearest atoms i and j , k_B is the Boltzmann constant, T is absolute temperature, $q_{ij} = \zeta_{ij}/z_1$, ζ_{ij} is the molecular acoustic partition function of the compound ij , $z_1 = 4$ is the coordination number of the nearest neighbours, u_{ijl} is the energy of interaction between the nearest cations of the i th and l th types with the intermediate anion of the j th type, u_{jim} is the energy of interaction between the nearest anions of the j th and m th types with the intermediate cation of the i th type, N_{ijl} is the number of i - j - l -type cation-anion-cation triads in the alloy and N_{jim} is the number of j - i - m -type anion-cation-anion triads in the alloy. The $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloy is considered as a canonical ensemble where the numbers of atoms N_{In} , N_{Ga} , N_{Sb} and N_{As} are given values. The number of cations is equal to the number of anions, $N = N_{\text{In}} + N_{\text{Ga}} = N_{\text{Sb}} + N_{\text{As}}$. According to thermodynamic equivalence of the statistical ensembles, one term in the sum (1) is significantly larger than the sum of all other terms [17]. Therefore, the maximal term will be used instead of sum (1).

The free energy of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys, in line with (1) and the thermodynamic equivalence of the ensembles, can be written as

$$\begin{aligned} F = -k_B T \ln Q &= \sum_{i,j,l,m=1}^2 \left(-k_B T \ln g \sigma_i^{N_i} \sigma_j^{N_j} q_{ij}^{N_{ij}} + u_{ij} N_{ij} + \frac{u_{ijl} N_{ijl} + u_{jim} N_{jim}}{2} \right) \\ &= \sum_{i,j,l,m=1}^2 \left(\frac{N_{ij}}{z_1} \mu_{ij}^0 + \frac{N_{ijl}}{2} w_{ij-lj} + \frac{N_{jim}}{2} w_{ij-im} - k_B T \ln g \right), \end{aligned} \quad (2)$$

where the values of g , N_{ij} , N_{ijl} and N_{jim} correspond to the maximal term in (1), $\mu_{ij}^0 = -k_B T \ln g \sigma_i \sigma_j q_{ij}^{z_1} + z_1 u_{ij} + z_2 (u_{ijl} + u_{jim})/2$, $z_2 = 12$ is the coordination number of the next nearest surroundings, $w_{ij-lj} = u_{ijl} - (u_{iji} + u_{ijl})/2$ is the parameter of interaction between the ij and lj compounds in the alloy.

3. The miscibility gap in the simple solution approximation

The simple solution approximation for the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys is based on the supposition of random distribution of cations and anions in their sublattices [6]. The number of configurations corresponding to the maximal term in (1) is close to the total number of configurations, that is written as

$$g = (N!)^2 \prod_{i,j=1}^2 (N_i!)^{-1} (N_j!)^{-1} = \frac{(N!)^2}{N_{\text{In}}! (N - N_{\text{In}})! N_{\text{Sb}}! (N - N_{\text{Sb}})!}.$$

The expressions for the numbers of pairs and triads are, respectively, given as

$$\begin{aligned} N_{ij} &= z_1 \frac{N_i N_j}{N}, & N_{iji} &= z_2 \frac{N_i^2 N_j}{2N^2}, & N_{jij} &= z_2 \frac{N_i N_j^2}{2N^2}, \\ N_{ijl} &= z_2 \frac{N_i N_j N_l}{N^2} & (i \neq l); & & N_{jim} &= z_2 \frac{N_i N_j N_m}{N^2} & (j \neq m). \end{aligned}$$

The heterogeneous system is considered as a canonical ensemble in which the phases are numbered $n = 1, 2$. The minimum condition for the free energy, obtained by the Lagrange method of underdetermined multipliers, leads to the system of equations

$$\frac{\partial F}{\partial N_1} = \frac{\partial F}{\partial N_2} = 0, \quad \frac{\partial F}{\partial N_{1\text{In}}} = \frac{\partial F}{\partial N_{2\text{In}}} = 0, \quad \frac{\partial F}{\partial N_{1\text{Sb}}} = \frac{\partial F}{\partial N_{2\text{Sb}}} = 0. \quad (3)$$

4. The miscibility gap in the quasichemical approximation

The quasichemical approximation is based on the assumption of random distribution of bonds between the nearest atoms [18]. The numbers of bonds are determined from the minimum condition for the free energy of an alloy. Thus, calculation of the free energy of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloy takes into account correlations in the arrangements of cations and anions. The numbers of the InAs, GaSb and GaAs bonds can be expressed in terms of the numbers of atoms and the number of InSb bonds as $N_{\text{InAs}} = z_1 N_{\text{In}} - N_{\text{InSb}}$, $N_{\text{GaSb}} = z_1 N_{\text{Sb}} - N_{\text{InSb}}$, $N_{\text{GaAs}} = z_1(N - N_{\text{In}} - N_{\text{Sb}}) + N_{\text{InSb}}$ [6]. In this case, the minimum condition for the free energy of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloy is given as [19]

$$\frac{dF}{dN_{\text{InSb}}} = 0.$$

The number of configurations and the numbers of triads can be written as

$$g = (N!)^2 \prod_{i,j=1}^2 \frac{(z_1 \frac{N_i N_j}{N})!}{N_i! N_j! N_{ij}!},$$

$$N_{ijl} = \frac{z_2}{2z_1^2} \frac{N_{ij} N_{lj}}{N_j}, \quad N_{jim} = \frac{z_2}{2z_1^2} \frac{N_{ij} N_{im}}{N_i}.$$

The free energy of the heterogeneous system is given as

$$F = \sum_{n=1}^2 \sum_{i,j,l,m=1}^2 \left\{ \frac{N_{nij}}{z_1} \mu_{ij}^0 + \frac{z_2}{2z_1} \left(\frac{N_{nij} N_{nim}}{N_{ni}} w_{ij-im} + \frac{N_{nij} N_{nlj}}{N_{nj}} w_{ij-lj} \right) - k_B T [(1 - z_1)(2N \ln N - N_{ni} \ln N_{ni} - N_{nj} \ln N_{nj})] \right\}$$

where the numbers of InSb pairs in the phases are determined by

$$\frac{\partial F}{\partial N_{1\text{InSb}}} = 0, \quad \frac{\partial F}{\partial N_{2\text{InSb}}} = 0. \quad (4)$$

Finally, the boundary of the MG is described by the system of equations (3) and (4).

5. Results and discussion

The MG of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys at temperatures of 500, 550, 600 and 650 °C was estimated in the simple solution and quasichemical approximations. These temperatures are conventional for LPHE of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys [1–3]. The data used in the calculations were taken from [20, 21]. Figure 1 shows the MG in both approximations. As is seen from figure 1, the MG estimated in the simple solution approximation is more extended than the MG calculated in the quasichemical one. The largest difference between the estimated MGs was found for the As-rich $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys. The difference between the MGs described in the simple solution and quasichemical approximations increases with temperature. This is a result of the diminution of the MG with rise of temperature.

The quasichemical and the simple solution approximations are equivalent to each other when x or y is equal to zero or unity. In this case, the alloy becomes ternary with a unique mixed sublattice. Concentrations of the bonds of the ternary alloy are expressed in terms of the concentrations of the atoms of the mixed sublattice. This means that the concentrations of the bonds do not depend on the arrangement of the atoms and the minimum condition for the free energy transforms into an identity. Therefore, the atoms of the mixed sublattice of the ternary alloy described in the quasichemical approximation are distributed randomly.

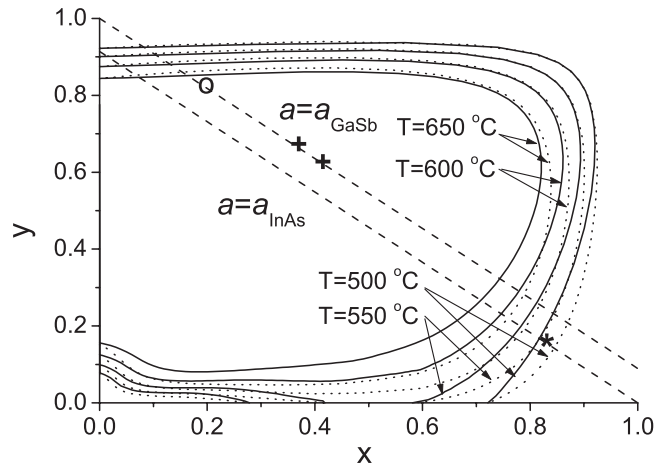


Figure 1. The MG of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys in the simple solution (dotted) and quasichemical (solid) approximations at temperatures of 500, 550, 600 and 650 °C. The dashed lines correspond to compositions of the alloys lattice matched to GaSb and InAs. The circle, asterisk and crosses show the experimental results from [1–3], respectively.

The compositions of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys grown by LPHE [1–3] are also shown in figure 1. The alloys grown on the GaSb substrates are inside the MG but the alloy grown on the InAs substrate is outside the MG. The alloys with compositions inside the MG were formed as a result of rapid crystallization of the GaSb-rich epitaxial layers from the melts with the large Ga and Sb concentrations. The large crystallization rate minimizes the dissolution of the substrate, which is one of the main problems of LPHE [22]. The As concentration in the melts in LPHE of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys is very small. The rate of growth of the InAs-rich alloy from a melt with a very small As concentration cannot be large. The small crystallization rate leads to the dissolution of the substrate. Therefore, LPHE for InAs-rich alloys inside the MG is difficult.

6. Conclusions

The miscibility gap of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y}$ alloys was described in the simple solution and quasichemical approximations of the regular solution model. The decomposed alloy was considered as a canonical ensemble. The largest difference between the miscibility gaps calculated in the two approximations was obtained for the As-rich quaternary alloys. In line with our theoretical estimations, the GaSb- and InAs-rich alloys grown by liquid phase heteroepitaxy are inside and outside the miscibility gap, respectively.

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