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Author(s)	Nakamura, K.; Mohri, T.; Ito, T.
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Theoretical Calculation of a Phase Diagram for InP-InSb Pseudo-Binary Alloy

K. NAKAMURA[1], T. MOHRI[1] and T. ITO[2]

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Abstract

We demonstrate the theoretically calculated phase diagram for InP-InSb pseudo-binary system both in the bulk and in the thin film. The bulk phase diagram is calculated besed on two schemes, nonempirical and semiempirical methods. The phase diagram for a thin film is, as an initial attempt, evaluated by adding an elastic energy term to the conventional semiempirical method. The elastic constraints from the substrate significantly affects the topology of the phase boundary.

I. INTRODUCTION

The phase stability of a semiconductor is of great importance in designing and manufacturing of electronic and optical devices. The phase diagram plays a key role in the analysis of the phase stability.

For the theoretical studies of a phase diagram in a bulk state, there have been two main directions developed in recent years. One is the nonempirical method[1-4] which combines electronic theory with statistical mechanics. The first-principles calculation has been known as the most extreme case in this category. The other is the semiempirical method[5,6] which has been developed by various people with different schemes. The common feature is that the models utilizes available experimental data within a mold of Bragg-Williams approximation[7] or regular solution model.

Contrary to the applicabilty of a muliticomponent system or even non-bulky system, the physical meanings of the parameters employed in the semiempirical methods are generally not clear. This is because the methods are based on the Bragg-Williams approximation which can not incorporate a wide range of atomic correlations. The deficiencies originated from a low level of the approximation are circumvented by the efficient parameterization.

The nonempirical method, on the other hand, is based on a quite salient physical basis, and since no fitting parameters are introduced to all equations resultant quantities have well established meanings. However, the shortcoming is the fact that the effect of local atomic relaxation[1,3,4] has been by no means taken into the rigorous framework of the model, which often leads to discrepancies of various aspects of a phase diagram.

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1) Department of Metallurgical Engineering, Hokkaido University, Sapporo 060 JAPAN
2) NTT LSI Laboratories, 3-1 Morinosato, Wakamiya, Atsugi 243-01 JAPAN

In this manner, the two methods have both advantages and disadvantages. One of the main aims of the present study is to compare the phase diagram for InP-InSb semiconductor alloy derived by the both methods.

So far, most of the investigation of a phase diagram, both experimental and theoretical, have been centered around a bulk state. In many cases, however, various devices are employed in the form of thin films under varying influences of the substrate. Therefore, the theoretical study of the constrained equilibria for a thin film is practically quite an important subject.

The stability of a thin film on a substrate is expected to be different from that of the bulk state in many ways. Among them is the elastic effect due to the substrate, which may shift its solubility line towards either a single-phase or a two-phases region. Forthermore, even a new phase which is not found in the bulk state may be stabilized. As an initial attempt to calculate a phase diagram in a thin film on a substrate, the semiempirical method is extended to incorporate elastic energy based on Johnson's ingredient[8]. The emphasis is placed on the variation of the topological feature of a phase boundary as a function of the substrate material.

II. CALCULATION PROCEDURE

II-A Nonempirical method

The heats of formation (internal energy) is generally expanded in the following form :

$$\Delta E=\sum_{i=0} \xi_i v_i, \qquad (1)$$

where ξ_i and v_i are, respectively, a correlation function and an effective interaction energy of an i-point cluster. The correlation functions ξ_i's which convey the information of atomic arrangement on the i-point cluster are variational parameters optimized in the course of minimization of the free energy functional under a given set of effective interaction energies v_i's. Hence the entire calculation starts with obtaining v_i's.

A III-V alloy with zincblend structure consists of two interpenetrating fcc sublattices. Then, for the InP-InSb pseudo-binary system, one sublattice is occupied by In alone, and the other lattice can be seen as a binary fcc system consisting of P and Sb. Based on this observation, the Cluster Expansion Method[9] for an fcc alloy system is applied to extract effective interaction v_i's up to 4-point cluster ($i=4$). The total energy $\Delta E^{(m)}(\gamma^{(m)}_{\min})$ of five kinds of ordered compounds $In_4P_{4-m}Sb_m$ (m=0, 1, 2, 3, 4), P_4 and Sb_4 with fcc structure, P_3Sb and PSb_3 with $L1_2$ structure and P_2Sb_2 with $L1_0$ structure, and the equilibrium lattice constant $\gamma^{(m)}_{\min}$ for each phase are calculated by the pseudopotential perturbation method[10,11].

Then, by combining bulk modulus which are either cited from experimental data[12] (InP and InSb) or interpolated (In_4P_3Sb, $In_4P_2Sb_2$, and In_4PSb_3), the dependency of the heat of formation of each ordered compound on the lattice constant can be fitted in the following form :

$$\varDelta E^{(\mathrm{m})}(r)=\frac{X^{(\mathrm{m})}}{r^{7.0}}-\frac{Y^{(\mathrm{m})}}{r^{3.5}}+Z^{(\mathrm{m})}, \tag{2}$$

where r is a lattice constant. This is because the three unknown parameters, $X^{(\mathrm{m})}$, $Y^{(\mathrm{m})}$ and $Z^{(\mathrm{m})}$, are uniquely determined from the knowledge of three independent quantities, $\gamma^{(\mathrm{m})}_{\mathrm{min}}$, $\varDelta E^{(\mathrm{m})}$ at $\gamma^{(\mathrm{m})}_{\mathrm{min}}$ and $B^{(\mathrm{m})}$.

The correlation function for an i-point cluster of an ordered compound m are determined *a pri · o'ri* since the atomic arrangement of completely ordered compound is uniquely fixed. By knowing both $\varDelta E^{(\mathrm{m})}(r)$ and the $\xi_i^{(\mathrm{m})}$'s for the five kinds of ordered compounds, the effective interaction energies up to tetrahedron-cluster ($i=0$, 1, 2, 3 and 4) can be extracted by the following matrix inversion :

$$v_i(\gamma)=\sum_{m=0}^{4}\varDelta E^{(\mathrm{m})}(\gamma)\{\xi_i^{(\mathrm{m})}\}^{-1}. \tag{3}$$

This method is the essence of the Cluster Expansion Method.

For the entropy expression $\varDelta S$, we employed the Tetrahedron-Octahedron approximation[13] of the Cluster Variation Method[14] ;

$$\varDelta S_{\mathrm{T-O}}=k_B\ln\frac{\{\prod_{jik}(\mathrm{z}_{ijk}\mathrm{N})!\}^8\{\prod_{i}(\mathrm{x}_i\mathrm{N})!\}}{\{\prod_{ij}(\mathrm{y}_{ij}\mathrm{N})!\}^6\{\prod_{ijkl}(\mathrm{w}_{ijkl}\mathrm{N})!\}^2\{\prod_{ijklmn}(\mathrm{v}_{ijklmn}\mathrm{N})!\}} \tag{4}$$

where k_{B} is the Boltzman constant and x_i, y_{ij}, z_{ijk}, w_{ijkl} and v_{ijklmn} are termed cluster probabilities which describe the probability of finding an atomic arrangement specified by subscript(s) on point, pair, triangle, tetrahedron and octahedron cluster, respectively. These variables can be related to the correlation functions in the follwing manner[13] :

$$\mathrm{x}_i=\frac{1}{2}(1+i\xi_1), \tag{5}$$

$$\mathrm{y}_{ij}=\frac{1}{2^2}\{1+(i+j)\,\xi_1+(ij)\,\xi_2\}, \tag{6}$$

$$\mathrm{z}_{ijk}=\frac{1}{2^3}\{1+(i+j+k)\,\xi_1+(ij+ik+jk)\,\xi_2+(ijk)\,\xi_3\}, \tag{7}$$

$$\begin{aligned}\mathrm{w}_{ijkl}=\frac{1}{2^4}\{&1+(i+j+k+l)\,\xi_1+(ij+ik+il+jk+jl+kl)\,\xi_2\\&+(ijk+ikl+ijl+jkl)\,\xi_3+(ijkl)\,\xi_4\},\end{aligned} \tag{8}$$

$$\begin{aligned}\mathrm{v}_{ijklmn}=\frac{1}{2^6}\{&1+(i+j+k+l+m+n)\,\xi_1\\&+[(n+l)(i+k+j+m)+(m+j)(i+k)]\,\xi_2\\&+(l+n)(j+m)(i+k)\,\xi_3+(ik+jm+ln)\,\xi_5\\&+[ik(j+l+n+m)+ln(i+j+k+m)+jm(i+k+l+n)\,\xi_6\\&+[ik(in+jl+lm+nm)+ln(ij+im+mk+jk)+mj(in+il+kl+kn)]\,\xi_7\\&+(ilkn+ijkm+jlmn)\,\xi_8\end{aligned}$$

$$+[jlmn(i+k)+ilkn(m+j)+ijkm(l+n)]\xi_9$$
$$+(ijklmn)\xi_{10}\}, \tag{9}$$

where i, j, k, l, m and n take $+1$ or -1 depending on A or B atom. Although the cluster probabilities and the correlation functions are convertible through the equations above, it is more convenient to employ the latter variables since they form an independent set of configuration variables.

The free energy expression in the present nonempirical method is, therefore, described as a function of temperature, correlation functions and a lattice constant.

$$\begin{aligned}\Delta F &= \Delta E - T\Delta S_{T-O}\\ &= f(T, \xi_1, \xi_2, \xi_3, \cdots, \xi_{10}, r)\end{aligned} \tag{10}$$

In order to attain a thermodynamic equilibrium state, eq. (10) has to satisfy the following two conditions :

$$\frac{\partial \Delta F}{\partial\{\xi_i\}}=0 \tag{11}$$

and

$$\frac{\partial \Delta E}{\partial V(r)}=-P_{ex} \tag{12}$$

where P_{ex} is the external pressure which is safely neglected to be zero for ambient atmosphere. The former condition is for a chemical equilibrium while the latter one is for a mechanical equilibrium.

Furthermore, in order to guarantee that the obtained equilibrium state is a stable one, the mechanical stability criterion[1] ;

$$-\frac{\partial^2 \Delta E}{\partial V^2(r)}=\frac{\partial P}{\partial V(r)}<0, \tag{13}$$

should be satisfied. When the above criterion is violated a small volume fluctuation drives the phase separation in order to reduce the free energy.

II-B Semiempirical method

II-B-1 Bulk system

The free energy formula in the semiempirical method is generally given in the following form :

$$\Delta G=\Omega_{AC-BC}(1-x)x+RT\{(1-x)\ln(1-x)+x\ln x\}, \tag{14}$$

where ΔG is the Gibbs free energy of an alloy at a compositon x ($A_{1-x}B_xC$), Ω_{AC-BC} is the interaction parameter which is, generally, parametrized in terms of composition and temperature based on experimental data. In the present study, the interaction parameter for InP-InSb was cited from the literature of Ishida et al[6].

The phase boundary is obtained by minimizing the Gibbs free energy with respect to the composition followed by the operation of the common tangent law.

II-B-2 Thin film system on a substrate

In the present study, it is assumed that the interface between a thin film (epitaxial layer) and a substrate is epitaxially bonded and that the substrate is elastically rigid. Then, the lattice constant of the epitaxial layer is determined by that of the substrate. When there exists a difference between the lattice constants of the thin film and that of the substrate material in their bulk states, strain arises in the epitaxial layer which increases the free energy.

Johnson[8] proposed to describe the epitaxial strain energy in the following way :

$$E_e = \frac{2\,\varepsilon^2 Y_{ijk}}{\rho_0{}'}, \tag{15}$$

where ε is the strain introduced by the substrate, ρ_0' is the density of lattice points in the sublattice and Y_{ijk} is the effective elastic modulus when the epitaxial layer is grown in [ijk] direction. The strain ε and the density ρ_0' are, respectivily, given as :

$$\varepsilon = \frac{r_e - Rs}{Rs}, \tag{16}$$

and

$$\rho_0{}' = \frac{\alpha}{Rs^3}, \tag{17}$$

where r_e is the lattice constant of the epitaxial layer in the stress-free state, Rs is the lattice constant of the substrate and α is the number of lattice points in the sublattice. The effective modulus for the grown orientation [100] is described as :

$$Y_{100} = \frac{(C_{11} - C_{12})\,(C_{11} + 2\,C_{12})}{C_{11}}, \tag{18}$$

where C_{ij} is the elastic constant[15].

The free energy of the epitaxial layer is, then, described in the following form :

$$\Delta G = \Omega_{AC-BC}(1-x)x + RT\{(1-x)\ln(1-x) + x\ln x\} + E_e \tag{20}$$

The equilibrium phase compositions at a given temperature are obtained again by the minimization of ΔG followed by the common tangent construction.

III RESULTS AND DISCUSSIONS

III-A Bulk system

The calculated phase diagram is demonstrated in Fig. 1. The solid and broken lines represent the results by nonempirical and semiempirical methods, respectively, which both demonstrate a miscibility type phase diagram. At the dilute limits, both results agree quite well and reproduces the experimental data (open circle) accurately. In the concentrated region, however, disagreements are emphasized. Since there are no experimental data available in this region, no definite conclusion could be made about the reliability of each result. However, it should be recalled that the nonempirical method does not take the local

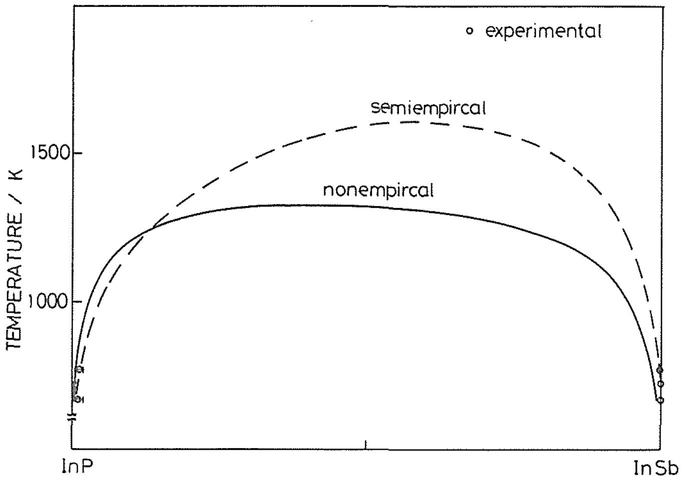

Fig. 1 Calculated phase diagram for the InP-InSb pseudo-binary system in the bulk. The solid and broken lines represent the results by the nonempirical and semiempirical methods[5,6], respectively. The open circles are the experimental results[6].

distortion effect into account. The shortcomings originated from this deficiency is expected to be emphasized in the concentrated region. On the other hand, Bragg-Williams approximation for the entropy expression of the semiempirical method obviously breaks down except in a dilute limit. Although the employed interaction energy parameter circumvented the defficiency to some extent, the applicability to a concentrated region is still open to question since the parameter is obtained from the experimental data basically in the dilute limit.

Based on the following consideration of the nonempirical method, the physical origin of the phase separation is, like other III-V pseudo-binary systems[3], attributed to the elastic energy contribution originated from the difference in the lattice constants of two constituent binary ordered compounds InP and InSb. As has been amply demonstrated in the previous publications[1,3], one can generally decompose the total heats of solution of random solid solution $E^{(\mathrm{rand})}$ into elastic energy contribution $E_{\mathrm{el}}^{(\mathrm{rand})}$ and chemical energy contribution $E_{\mathrm{chem}}^{(\mathrm{rand})}$,

$$E^{(\mathrm{rand})}(\mathrm{x},\ r)=\Sigma v_i(r)\,\xi_1^i(\mathrm{x}), \tag{21}$$

$$E_{\mathrm{el}}^{(\mathrm{rand})}(\mathrm{x},\ r^{(\mathrm{rand})})=(1-\mathrm{x})E^{(\mathrm{In_4P_4})}(r^{(\mathrm{rand})})+\mathrm{x}E^{(\mathrm{In_4Sb_4})}(r^{(\mathrm{rand})}) \tag{22}$$

and

$$E_{\mathrm{chem}}^{(\mathrm{rand})}(\mathrm{x},\ \gamma^{(\mathrm{rand})})=E^{(\mathrm{rand})}(\mathrm{x},\ r^{(\mathrm{rand})})+E_{\mathrm{el}}^{(\mathrm{rand})}(\mathrm{x},\ r^{(\mathrm{rand})})\quad . \tag{23}$$

In the eq. (21), it is noted that the mulitibody correlation is given as a simple product of point correlation, which is the definition of a random state. The physical meaning $E^{(\mathrm{rand})}$ (eq. (22))

is understood as the energy required to expand a smaller compound (InP) and to compress a larger compound (InSb) to the equilibrium size of a complete random solid solution ro that two separated phases, $(In_4P_4)_{1-x}$ and $(In_4Sb_4)_x$, are formed on a lattice of which lattice constant is the equilibrium of a random solid solution. The chemical energy is the difference between the total energy $E^{(rand)}$ obtained by pseudopotential calculation and the elastic energy contribution $E_{el}^{(rand)}$. The results are plotted in Fig. 2. The reference energy is the concentration average of the heats of formation of the two binary ordered phases. The broken, dot-broken and solid lines indicate the elastic energy contribution, the chemical energy contribution and the heats of formation (total energy) of complete random solid solution, respectively. One can see that the system has a large positive elastic energy which contributes to drive a system towards phase separation. It should be stressed that the big chemical energy contribution implies that the system has an inherently large chemical driving force of mixing.

It shoud be noted that the semiempirical method produces the narrower solid solution region in the InSb side while the nonempirical method yields nearly symmetric phase boundary. As was pointed out in the previous publications[2,3], the following consideration on the asymmetry of a phase boundary may be generally applied to many systems calculated by the nonempirical method. When a solute element of a smaller size dissolves into a matrix of a larger element, the solute element is expanded to the size of the larger element since the nonempirical method assumes a rigid lattice without allowing local lattice relaxation.

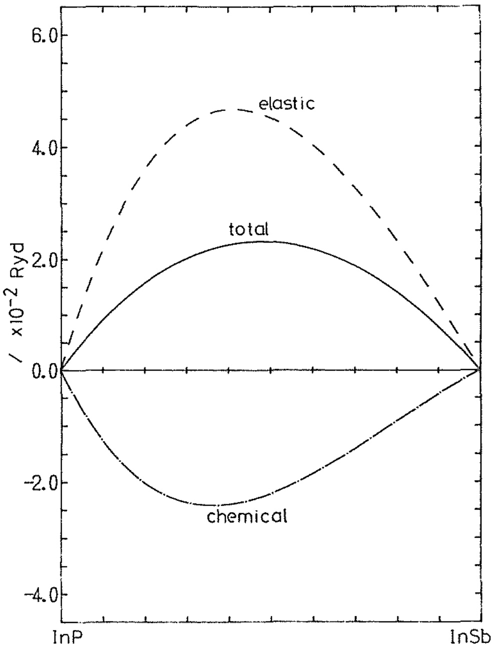

Fig. 2 Separation of the total heats of formation of random solid solution $E^{(rand)}$ into elastic energy contribution $E^{(rand)}$ and chemical energy contribution $E^{(rand)}$.

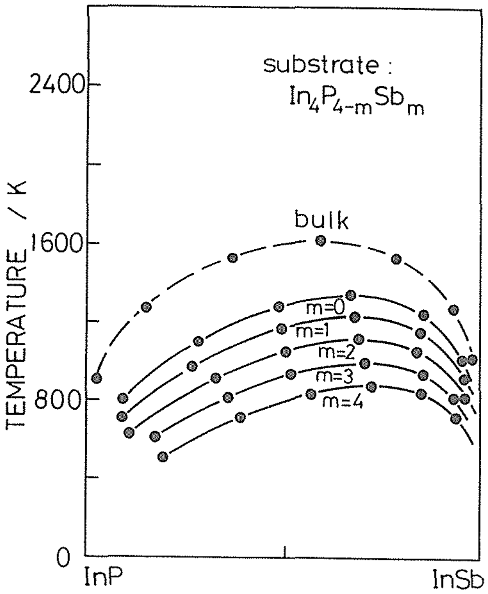

Fig. 3 Calculated phase diagram of the epitaxial layer for InP-InSb pseudo-binary system on the substrate of $In_4P_{4-m}Sb_m$ (m = 0, 1, 2, 3 and 4) when the grown direction is [100]. The broken line represents the result for the bulk state.

While for a solute element of a larger size dissolving into a matrix of a smaller element, the solute element is compressed into the size of the smaller element. It has been generally confirmed for a solid phase that compression requires more energy than expansion, which suggests that the latter process expends more energy. Hence the general rule deduced is that the phase field of the solid solution on the side of smaller element is narrower than that of the larger element. The resultant phase diagram of the nonempirical method certainly obeys this rule. It is again pointed out that such a consideration, however, may be broken down when a local relaxation is taken into account.

III-B Thin film system on a substrate

The calculated phase diagrams of an epitaxial layer grown in [100] for various substrates $In_4P_{4-m}Sb_m$ (m=0, 1, 2, 3 and 4) are demonstrated in Fig. 3. In the figure the phase boundary for a bulk is demonstrated for comparison. One can see that the miscibility gap is narrowed down by the elastic constraint of the substrate.

In order to clarify the effect of elastic energy, the total energies for bulk and thin film

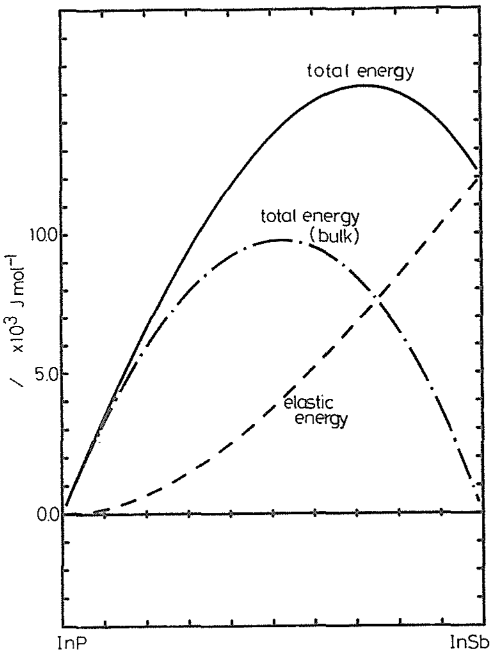

Fig. 4(a) Total energy and elastic energy for the epitaxial layer of InP-InSb pseudo-binary system on the substrate of InP at T=OK for the [100] growth direction. The solid and broken lines represent the total energy and the elastic energy, respectively. The dot-broken line is the total energy in the bulk state. The reference energy is the concentration average of the heats of formation of InP and InSb in the bulk state.

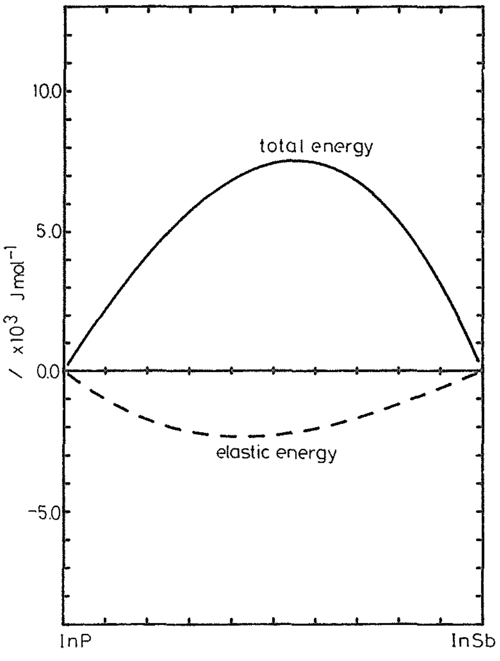

Fig. 4(b) Total energy (solid line) and elastic energy (broken line) for the epitaxial layer of InP-InSb pseudo-binary system on the substrate of InP. The reference energy is the concentration average of the heats of formation of InP and InSb under the constraint of the InP substrate.

on InP substrate at T=OK are shown in Fig. 4(a). One can see that the total energy is greatly increased in the InSb side. Shown in Fig. 4(b) are cases when the concentration average of the heats of formation of InP and InSb (segregation limit) under the constraint of the InP substrate is taken as a new reference state. An asymetry is certainly pronounced, which leads to the pronounced asymmetry of the phase boundary in Fig. 3.

IV SUMMARY

We calculated the phase diagrams of the InP-InSb pseudo-binary system in the bulk state by nonempirical and semiempirical methods. Both methods yield a phase separation type phase diagram. It is revealed by the nonempirical method that the elastic energy contribution due to the size difference of InP and InSb causes the phase separation. The semi-empirical method is modified to calculate the phase diagram in a thin film state. It is shown that the elastic constraint due to the substrate drives a system towards a solid solution.

Although the semiempirical method is efficient to draw a phase diagram, the physical origin of the calculated quantities are hardly clarified. It remains as a future task to expand the nonempirical method to a thin film layer in order to grasp the physics of phase equilibria of an epitaxial layer.

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