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PREDICTION OF THERMODYNAMIC PROPERTIES FOR Ga-Al-As-In COMPOUND SIMICONDUCTOR SYSTEM WITH CHOU MODEL

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Abstract

The application of the new geometrical model (Chou model), which can avoid the arbitrary choice for models and asymmetrical components, is more reasonable and convenient than other symmetrical (or asymmetrical) models. The new geometrical model is easy to develope as a computer program in calculating thermodynamic properties for a multicomponent system based on relative binary systems. With this model, the excess Gibbs free energies of mixing for Ga-Al-As-In compound simiconductor system have been calculated, and the results are compared with that of previous typical models.

Keywords: thermodynamic property, new geometrical model, Ga-Al-As-In, multicomponent system

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1. Introduction

The group III-V compound semiconductors and their solid solutions are important materials used in opto-electronic and high speed electronic device applications. The fabrication of these devices can involve processes that require contact between the solid and a fluid phase at near equilibrium condition. Examples of processes that involve contact between the solid and liquid phases include bulk crystal growth and liquid phase epitaxy, and between the solid and vapour phases include chemical vapour deposition, molecular beam epitaxy and rapid thermal annealing. Therefore, knowledge of the phase diagram and thermodynamic properties for these semiconductors system is important for providing boundary condition in the analysis of a variety of processing steps.

The collection, assessment and recommendation of thermodynamic properties for a material system of this size are significant tasks. Though databases have been previously published by several investigators for group III-V systems, additional experimental measurements have been reported for many systems that modify the conclusions of the previous databases, it is not enough for the recent research work and fabrication. In addition to these databases, there have been several excellent assessments of selected systems reported in the literature. Giving an important multicomponent is difficult since different solution models and reference state of properties have often been used.

Recently, Chou[1] established a new geometric model for calculating the thermodynamic properties of liquid multicomponent systems from corresponding binaries. It can overcome nearly all the defects appearing in previous traditional geometric models [2, 3]. And it is expected to apply in some liquid multicomponent systems, which is difficult to select symmetrical (or asymmetrical) geometric model and asymmetrical component. In this work, the new geometric model was applied in prediction for the thermodynamic properties of Ga-Al-As-In compound simiconductor system. Also, the results are compared with that of previous typical geometrical models.

2. New geometric model

Firstly, Chou defined a quantity η_i that is called the "deviation sum of squares",

$$\eta_1 = \int_0^1 \left(\Delta G^{\mathrm{E}}_{1-2} - \Delta G^{\mathrm{E}}_{1-3}\right)^2 \mathrm{d}X_{1(1\text{-}2)} \tag{1}$$

$$\eta_2 = \int_0^1 \left(\Delta G^{\mathrm{E}}_{2-1} - \Delta G^{\mathrm{E}}_{2-3}\right)^2 \mathrm{d}X_{2(2\text{-}3)} \tag{2}$$

$$\eta_2 = \int_0^1 \left(\Delta G^{\mathrm{E}}_{2-1} - \Delta G^{\mathrm{E}}_{2-3}\right)^2 \mathrm{d}X_{2(2\text{-}3)} \tag{3}$$

Where $\Delta G^E_{1\text{-}2}$, $\Delta G^E_{2\text{-}3}$ and $\Delta G^E_{3\text{-}1}$ represent the excess Gibbs energies of mixing of binary solution 1-2, 2-3 and 3-1, respectively; $X_{1(1\text{-}2)}$, $X_{2(2\text{-}3)}$ and $X_{3(3\text{-}1)}$ indicate the mole fractions of component 1 in 1-2, 2 in 2-3 and 3 in 3-1, respectively.

Then another quantity $\xi_{i\text{-}j}$ introduced, the so called "similarity coefficient" which is defined as

$$\xi_{1-2} = \frac{\eta_1}{\eta_1 + \eta_2} \tag{4}$$

$$\xi_{2-3} = \frac{\eta_2}{\eta_2 + \eta_3} \tag{5}$$

$$\xi_{3-1} = \frac{\eta_3}{\eta_3 + \eta_1} \tag{6}$$

On the basis of the above definition, the following binary compositions will be selected for this new model,

$$X_{1(1-2)} = x_1 + \xi_{1-2} x_3 \tag{7}$$

$$X_{2(2-3)} = x_2 + \xi_{2-3} x_1 \tag{8}$$

$$X_{3(3-1)} = x_3 + \xi_{3-1} x_2 \tag{9}$$

where x_1, x_2 and x_3 denote the mole fractions of component 1, 2 and 3 in the ternary.

This new model differs from all other models on its special selection of binary compositions that are closely related to the ternary system considered. However, all current models select the binary compositions in three binaries in an unchangeable manner.

In a multi-component system, $\Delta G^{E}_{i\text{-}j}$ is expressed as the following with Ridlich-Kister [4] multinomial:

$$\Delta G^{\mathrm{E}}_{i-j} = X_{i(i-j)} X_{j(i-j)} \sum_{v}^{n} L^{v}_{i-j} \left(X_{i(i-j)} - X_{j(i-j)} \right)^{v} \tag{10}$$

Where $\Delta G^{E}_{i\text{-}j}$ is the excess Gibbs energy of mixing of binary solution i-j, $X_{i(i\text{-}j)}$ and $X_{j(i\text{-}j)}$ denote the component i and j mole fractions in the binary i-j, respectively. $L^{v}_{i\text{-}j}$ represents the interaction parameter for binary i-j, which is independent of composition but dependent on temperature.

Combining Eqs. (1) ~ (10), the excess Gibbs energy of mixing ΔG^{E} can be obtained for a multicomponent system from relative binaries:

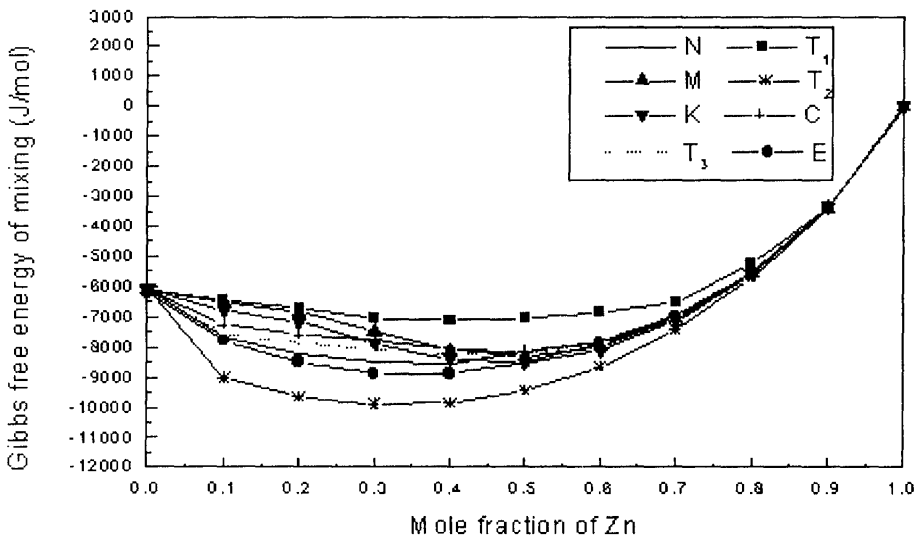
$$\Delta G^{\mathrm{E}} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{x_i x_j}{X_{i(i-j)} X_{j(i-j)}} \Delta G^{\mathrm{E}}_{i-j} \tag{11}$$

3. Results and Discussion

With the new generation solution model (Chou model) and symmetrical (or asymmetrical) models, a computer program has been developed. As the results of verification, the calculated molar Gibbs free energy of mixing for the asymmetrical system Ag-Sn-Zn (Ag taken as the asymmetrical component) at 900K are shown in Fig.1 [5-7]. For comparison, the results of some typical symmetrical model (Kohler, Colinet, Muggianu) or asymmetrical model (Toop model) as well as the experimental data[8] are also included. From results, it can be seen that the line calculated from new model is much more similar the experimental data than that predicted by other typical symmetrical models or asymmetrical models and results are

very different due to the selections of various components as asymmetrical components.

In multicomponent Ga-Al-As-In system, the molar Gibbs free energies of mixing for all sub-binaries in this system at 2100K are shown in Fig. 2 for comparison. The similarity coefficients for all sub-binaries in this system at 2100K are shown in Table 1, respectively. And the molar excess Gibbs free energies of mixing for liquid Ga-Al-As-In four component system has been calculated (Fig. 3).



N-New model, T_1-Toop model (Sn as a asymmetrical component), M-Muggianu model T_2-Toop model (Zn as a asymmetrical component), K-Kohler model, C-Colinet model T_3-Toop model (Ag as a asymmetrical component), E-Experimental data.

Fig. 1. Comparison between the measured and the calculated molar Gibbs Energy of mixing in the ternary Ag-Sn-Zn (Ag/Sn=1).

It can be seen that Al-As-Ga-In system is an asymmetrical system from (Fig.2) the comparison of excess Gibbs free energy of mixing for sub-binaries in Al-As-Ga-In system at 2100K. So the asymmetrical model should be

used, rather than the symmetrical one. But in this case, it is not clear which component is asymmetrical one. From the Fig.3, the results when As or In as the asymmetrical component meet the new model very well, and others will lead to a little deviation due to wrong man-made selection for asymmetrical component.

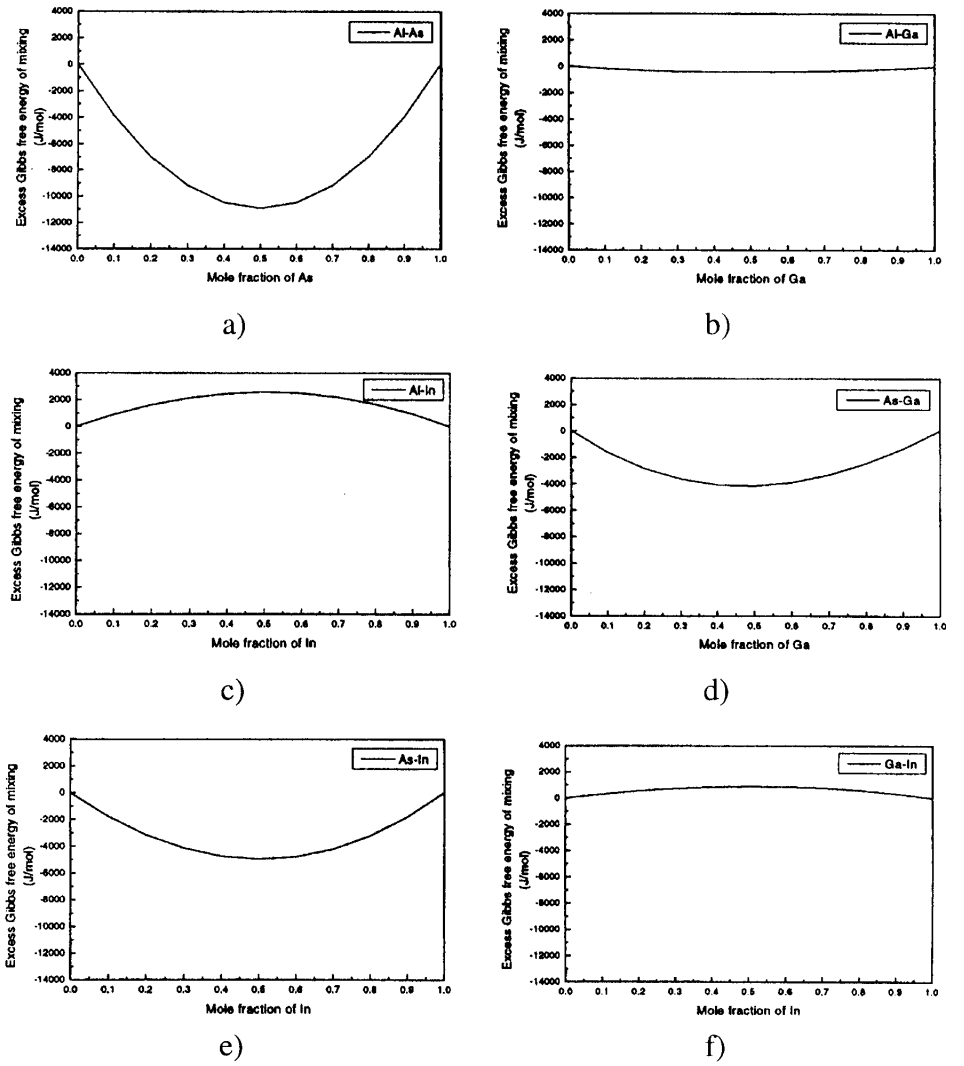


Fig.2. The comparison of excess Gibbs free energy of mixing for sub-binaries in Al-As-Ga-In system at 2100K.

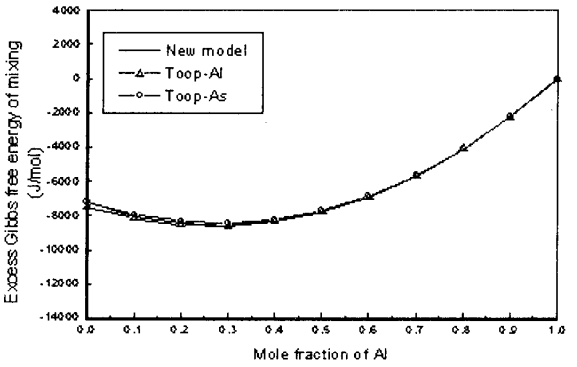
Table 1. The similarity coefficient in Al-As-Ga-In system at 2100K.

Similarity coefficient	Al-As-Ga-In (1-2-3-4)	As-Ga-In-Al (1-2-3-4)	Ga-In-Al-As (1-2-3-4)	In-Al-As-Ga (1-2-3-4)
12-3	0.71547	0.01532	0.38981	0.23507
12-4	0.83511	0.74320	0.44416	0.23613
13-2	0.87919	0.01228	0.16491	0.60734
13-4	0.83893	0.39226	0.12081	0.98772
14-2	0.76403	0.28453	0.98468	0.61019
14-3	0.75982	0.16575	0.25680	0.55584
23-1	0.74320	0.44416	0.23613	0.83425
23-4	0.01532	0.38981	0.23507	0.71547
24-1	0.38998	0.12081	0.98772	0.83509
24-3	0.01228	0.16491	0.60734	0.87919
34-1	0.37788	0.23507	0.71547	0.01532
34-2	0.44416	0.23613	0.83425	0.74320

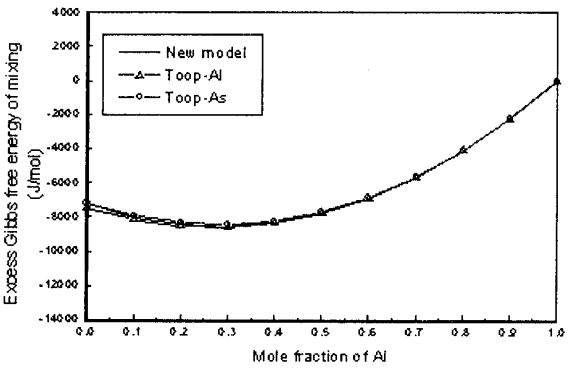
Obviously, it is very important for a system to select an appropriate model or asymmetrical component in calculation. In addition to the cases which can be described by symmetrical and asymmetrical models, there are some other cases which meet neither symmetrical conditions nor current asymmetrical condition. In this particular situation, all sub-binaries have different selected composition, which can still be described by this new model. In other words, this new model can be used in more practical systems than symmetric plus asymmetric model.

4. Conclusion

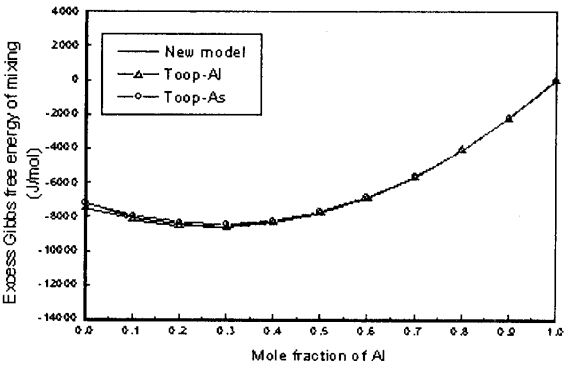
With the new geometrical model (Chou model) and symmetrical (or asymmetrical) models, a computer application program has been developed; with the calculation of molar Gibbs free energies of mixing for Ag-Sn-Zn



a) ($x_{As}=x_{Ga}=x_{In}$)



b) ($x_{Ga}=x_{In}=x_{Al}$)



c) ($x_{In}=x_{Al}=x_{As}$)

Fig.3. The excess Gibbs free energy of mixing curves for Ga-Al-As- In system at 2100K.

ternary system at 900K, the comparison between new geometrical model and previous typical models was made. And the results show the new geometrical model is reliable.

The molar excess Gibbs free energies of mixing for liquid compound semiconductor Ga-Al-As-In four component system have been calculated. The results show that the application of the new geometrical model is more reasonable and convenient than other symmetrical (or asymmetrical) geometrical models.

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