Thermodynamic Calculation of Phase Equilibria in As-Fe-In Ternary System Based on CALPHAD Approach

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Thermodynamic calculation of phase equilibria in As-Fe-In ternary system is performed based on Calphad approach, directing a special attention to fabrication process of Fe/InAs hybrid structure for spin injection device. For this, the thermodynamic assessment of Fe-In binary system is first carried out utilizing reported experimental data. Then, the liquidus surface of the ternary system and invariant reactions are calculated. The isothermal sections in low temperature region are presented and discussed in the light of the optimization of the growth temperature of Fe film on InAs substrate during the fabrication process. [doi:10.2320/matertrans.MER2008437]

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1. Introduction

Spin injection from ferromagnetic metal into semiconductor is one of the key issues in emerging field of spintronics.^{1–3)} Fe/InAs hybrid structure has attracted attention as a candidate for realizing high spin injection efficiency.^{4–7)} The spin injection efficiency is critically dependent on the interface quality of the hybrid structure. Considerable efforts have been devoted to optimize the process parameters during Molecular Beam Epitaxy (MBE) growth of Fe film on the semiconductors.^{4–7)} In early studies on the Fe growth on GaAs substrate, the growth temperature between 420 and 450 K was chosen so that the Fe film can grow on the GaAs without forming defects of high density. However, it was reported that the epitaxial growth of Fe film on the InAs substrate at 450 K involves an interface reaction, resulting in the formation of a compound at the interface and, consequently, low spin injection efficiency was observed.⁷⁾ There have not been any conclusive data identifying the type of the reaction at the interface. On the other hand, the MBE growth of Fe film on the InAs at 296 K leads to a clear interface, i.e., the interface without the formation of compound and high spin injection efficiency of 30–40% was realized.⁷⁾ It should be noted that the optimization of the fabrication process parameters of the hybrid structure has been currently attempted by a trial and error.

The information on the phase equilibria is fundamental in the development of electronic devices.^{8–11)} Especially, the isothermal section for metal/III-V semiconductor in low temperature region is of great importance in understanding and predicting the interface reaction during the fabrication process, as discussed in detail for metal/GaAs system.⁹⁾ The isothermal section for As-Fe-In ternary system at 300 K has been estimated from the formation enthalpy of the compounds based on the Miedema's model.¹²⁾ In order to obtain the further information about the phase equilibria associated with Fe/InAs hybrid structure, in this work, the isothermal sections at higher temperature are clarified based on the Calphad approach.¹³⁾ The Calphad is an empirical approach in which the thermodynamic quantities of the system are

described through simple phenomenological expressions for the Gibbs energies of all the phases. The Calphad method based on well-established thermodynamic parameters enables a precise description of the phase equilibria of multi-component system. To this end, we performed the thermodynamic modeling for the As-Fe binary system based on the first-principles total energy calculations for the As-Fe compounds.¹⁴⁾ The thermodynamic modeling of the As-In system was reported in the early work,¹⁵⁾ while the Fe-In system has not been subjected to the thermodynamic assessment. In this study, therefore, we first carry out the thermodynamic modeling for the Fe-In binary system and then perform the calculation for the ternary system, demonstrating the isothermal sections associated with the fabrication process of Fe/InAs hybrid structure.

2. Calphad Approach

In this section, we present the thermodynamic modeling for the As-Fe-In ternary system. For precise description of phase equilibria of the ternary system, it is indispensable to develop the thermodynamic descriptions of the binary edge systems with a high accuracy based on well-established experimental data. As already mentioned, the binary As-In and As-Fe systems have been subjected to the detailed thermodynamic assessments.^{14,15)} In this study, we perform the modeling for the Fe-In binary system.

2.1 Fe-In binary system

The phase equilibria of the Fe-In binary system have been reviewed.¹⁶⁾ The phase equilibria of this system are characterized by existence of a miscibility gap in the liquid, monotectic reaction $L_1 \leftrightarrow (\delta\text{Fe}) + L_2$, catatctic reaction $(\delta\text{Fe}) \leftrightarrow (\gamma\text{Fe}) + L_2$, peritectic reaction $(\gamma\text{Fe}) + L_2 \leftrightarrow (\alpha\text{Fe})$ and eutectic reaction $L_2 \leftrightarrow (\alpha\text{Fe}) + (\text{In})$. The monotectic temperature was measured in the early experimental works.^{17–19)} The solubility of Fe in the In-rich liquid phase was reported^{17,20)} and the solubilities of In in (δFe) , (γFe) and (αFe) were also determined.^{17,19)} We employed these experimental data in the present assessment.

The molar Gibbs energy for solution phases such as liquid, (α Fe) and (γ Fe) is expressed by the following equation,

$$G^\phi = x_{\text{Fe}} G_{\text{Fe}}^{0,\phi} + x_{\text{In}} G_{\text{In}}^{0,\phi} + RT(x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{In}} \ln x_{\text{In}}) + x_{\text{Fe}} x_{\text{In}} \sum_{v=0} L_{\text{Fe,In}}^{\phi,v} (x_{\text{Fe}} - x_{\text{In}})^v, \quad (1)$$

where R is the gas constant, x_i with $i = \text{Fe}$ and In is the molar fraction of Fe and In, respectively. $G_i^{0,\phi}$ is the Gibbs energy function for pure element i in phase ϕ , which was taken from the SGTE compilation by Dinsdale²¹⁾ and $L_{\text{Fe,In}}^{\phi,v}$ is the v^{th} Redlich-Kister parameter. The magnetic energy contribution is taken into account in the model for (α Fe) and (γ Fe) solution phases on the basis of the method developed by Hillert and Jarl.²²⁾ The Gibbs energies thus described are quantified based on the experimental data for the phase boundaries.

2.2 As-Fe-In ternary system

The crystal structures of solid phases in this ternary system are summarized in Table 1. No ternary compounds are reported in this system.²³⁾ The experimental data available for this ternary system is the one only for the phase equilibria on the section InAs-AsFe by slow directional solidification experiment.²⁴⁾ The thermal signal was detected at $T = 1203 \pm 2 \text{ K}$ which was confirmed to be a reaction $\text{L} \leftrightarrow \text{InAs} + \text{AsFe}$ by means of the microstructural observation and X-Ray Diffraction (XRD) analysis. Although the InAs-AsFe section was supposed to consist of a simple eutectic pseudobinary system with the eutectic reaction, it was pointed out that there possibly exists the huge liquid miscibility gap extending from the binary Fe-In system into ternary.²³⁾

For the calculation of the ternary system, we employed the thermodynamic descriptions of As-In¹⁵⁾ and As-Fe¹⁴⁾ binary edge systems in addition to the one for Fe-In system obtained in this study. As described above, there is only the experimental data on InAs-AsFe section available in this

Table 1 Crystal structures of solid phases in As-Fe-In system. The last column represents the sublattices and constituent for the Gibbs energy model. The Gibbs energy for (α Fe) and (δ Fe) phases are described with the single solution model.

Phase name	Pearson symbol	Space group	Strukturbericht designation	Prototype	Sublattices and constituent
α As	<i>hR2</i>	<i>R$\bar{3}m$</i>	A7	α As	(As)
(α Fe)/(δ Fe)	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W	(As, Fe, In)
(γ Fe)	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	A1	Cu	(As, Fe, In)
In	<i>tI2</i>	<i>I4/mmm</i>	A6	In	(In)
InAs	<i>cF8</i>	<i>F$\bar{4}3m$</i>	B3	ZnS	(In)(As)
As ₂ Fe	<i>oP6</i>	<i>Pnnm</i>	C18	FeS ₂	(As) ₂ (Fe)
AsFe	<i>oP8</i>	<i>Pnma</i>	B31	MnP	(As)(Fe)
As ₂ Fe ₃	—	—	—	—	(As, Va) _{0.75} (Fe)
AsFe ₂	<i>tP6</i>	<i>P4/nmm</i>	C38	Cu ₂ Sb	(As)(Fe) ₂

ternary system and, therefore, we assume no ternary solubility in the compounds and did not introduce any ternary parameters into the model for solution. The molar Gibbs energy for solution phases in the ternary system is expressed as follows,

$$G^\phi = x_{\text{As}} G_{\text{As}}^{0,\phi} + x_{\text{Fe}} G_{\text{Fe}}^{0,\phi} + x_{\text{In}} G_{\text{In}}^{0,\phi} + RT(x_{\text{As}} \ln x_{\text{As}} + x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{In}} \ln x_{\text{In}}) + x_{\text{As}} x_{\text{Fe}} \sum_{v=0} L_{\text{As,Fe}}^{\phi,v} (x_{\text{As}} - x_{\text{Fe}})^v + x_{\text{Fe}} x_{\text{In}} \sum_{v'=0} L_{\text{Fe,In}}^{\phi,v'} (x_{\text{Fe}} - x_{\text{In}})^{v'} + x_{\text{As}} x_{\text{In}} \sum_{v''=0} L_{\text{As,In}}^{\phi,v''} (x_{\text{As}} - x_{\text{In}})^{v''}, \quad (2)$$

where x_{As} is the molar fraction of As, $G_{\text{As}}^{0,\phi}$ is the Gibbs energy function for As in phase ϕ and $L_{i,j}^{\phi,v}$ is the v^{th} Redlich-Kister parameter between i and j elements in phase ϕ . The thermodynamic parameters in this system are summarized in Table 2. It should be pointed out that all the compounds except for As₂Fe₃ were modeled as the line compound and

Table 2 Thermodynamic parameters.

Liquid	$L_{\text{As,Fe}}^{L,0} = -83810.9 + 3.0716T$	$L_{\text{As,Fe}}^{L,1} = 50261.1 - 4.6947T$
	$L_{\text{As,Fe}}^{L,2} = 75085.7 - 45.1907T$	$L_{\text{As,Fe}}^{L,3} = -46496.7$
	$L_{\text{Fe,In}}^{L,0} = 52838.5 - 5.5432T$	$L_{\text{Fe,In}}^{L,1} = 3999.9$
	$L_{\text{As,In}}^{L,0} = -15851 - 11.2705T$	$L_{\text{As,In}}^{L,1} = -1219.5$
(α Fe)/(δ Fe)	$L_{\text{As,Fe}}^{\text{bcc},0} = -122879.9 + 67.9395T$	$L_{\text{As,Fe}}^{\text{bcc},1} = -3248.55 + 45.8837T$
	$L_{\text{As,Fe}}^{\text{bcc},2} = 23365.2$	
	$L_{\text{Fe,In}}^{\text{bcc},0} = 19098.8 + 22.3585T$	
	$L_{\text{As,In}}^{\text{bcc},0} = 80T$	
(γ Fe)	$L_{\text{As,Fe}}^{\text{fcc},0} = -80000 + 13.5T$	
	$L_{\text{Fe,In}}^{\text{fcc},0} = 23682.9 + 21.5678T$	
	$L_{\text{As,In}}^{\text{fcc},0} = 80T$	
InAs	$G^{\text{InAs}} = -73057.2 + 230.919T - 45.1879T \ln T - 0.00773T^2 + 69438T^{-1} + 1.41806 \times 10^{-7}T^3$	
As ₂ Fe	$G^{\text{As}_2\text{Fe}} = -37236.8 + 10.9657T + (2/3) \cdot G_{\text{As}}^{0,\text{rhombo}} + (1/3) \cdot G_{\text{Fe}}^{0,\text{bcc}}$	
AsFe	$G^{\text{AsFe}} = -37991.2 + 122.3339T - 22.1461T \ln T - 4.6066 \times 10^{-3}T^2 - 7.205 \times 10^{-7}T^3$	
AsFe ₂	$G^{\text{AsFe}_2} = -28919.1 + 3.9343T + (1/3) \cdot G_{\text{As}}^{0,\text{rhombo}} + (2/3) \cdot G_{\text{Fe}}^{0,\text{bcc}}$	
As ₂ Fe ₃	$G_{\text{Fe:As}}^{0,\text{As}_2\text{Fe}_3} = -40812.6 - 5.5208T + 0.75G_{\text{As}}^{0,\text{rhombo}} + G_{\text{Fe}}^{0,\text{bcc}}$	
	$G_{\text{Fe:Va}}^{0,\text{As}_2\text{Fe}_3} = 5000 - 0.3383T + G_{\text{Fe}}^{0,\text{bcc}}$

Fig. 1 (a) Calculated phase diagram of Fe-In system. (b) Enlargement of the Fe-rich part.

the Gibbs energies for InAs and AsFe were described with absolute reference state and those for As_2Fe and AsFe_2 were described with floating reference state. The thermodynamic state of As_2Fe_3 was modeled by Compound Energy Formalism (CEF). The definition of parameters for these compounds used in Table 2 and the detail of the Gibbs energy models for each phase can be found in the previous reports.^{14,15)}

3. Results and Discussions

The phase diagram for the binary Fe-In system calculated from the present model is shown in Fig. 1 where the experimental data for the phase boundaries are also indicated. It can be seen that the calculated result is in reasonable agreement with the experimental data, especially those obtained by Dasarathy,¹⁹⁾ and Mal'yugin *et al.*²⁰⁾ The calculated invariant reactions are summarized in Table 3.

The calculated liquidus surface for the As-Fe-In ternary system is shown in Fig. 2 with the isothermal lines at an interval of 100 K. The liquid composition in the invariant reaction is denoted with a symbol. The reaction type, the temperature and its symbol used in Fig. 2 are summarized in Table 4. The thin dashed line in Fig. 2 represents the isothermal lines for liquid miscibility gap. It is noted that the As-rich part corresponds to the metastable phase diagram, since the stable state of As in these temperature range at

Table 3 Calculated invariant reactions in Fe-In system.

Reaction	Temperature (K)	Composition of phases involved in the reaction, x_{In}		
$L \leftrightarrow L_1 + L_2$	2423	0.4258		
$L_1 \leftrightarrow (\delta\text{Fe}) + L_2$	1744	0.0523	0.0092	0.903
$(\delta\text{Fe}) \leftrightarrow (\gamma\text{Fe}) + L_2$	1617	0.0085	0.0067	0.9388
$(\gamma\text{Fe}) + L_2 \leftrightarrow (\alpha\text{Fe})$	1195	0.0040	0.9904	0.0049
$L_2 \leftrightarrow (\alpha\text{Fe}) + \text{In}$	429	~ 1.0	~ 0.0	~ 1.0

Fig. 2 Calculated liquidus surface. The bold solid lines represent the monovariant lines. The thin solid lines indicate isotherms at an interval of 100 K. The isothermal lines of liquid miscibility gap are also demonstrated by the dashed thin line. The As-rich part corresponds to the metastable phase diagram, since the stable state of As in these temperature range is vapor phase. The phase name in the figure specifies the primary crystallizing phase in the corresponding field.

normal pressures is vapor phase. One can see that the large miscibility gap region extends from the binary Fe-In edge into the ternary as pointed out in the review report.²³⁾ The invariant reaction points in the vicinity of the binary edge systems are enlarged in Fig. 3. It is noted that there exist three ternary monotectic reactions in this system and four types of maximum temperatures for degenerated reactions. Especially, the maximum temperatures, m_1 , m_2 and m_4 are located along the section at $x_{\text{As}} = 0.5$ between InAs and AsFe compounds. The vertical section between InAs and AsFe compounds is shown in Fig. 4. The experimental data,²⁴⁾ which is only the data available in this ternary system, is also indicated in Fig. 4. The calculated result demonstrates that in this section, the eutectic reaction $L \leftrightarrow \text{AsFe} + \text{InAs}$ occurs at 1205 K. This is in excellent agreement with the experimental finding²⁴⁾ by means of the thermal analysis, microstructural observation and XRD analysis. It should be pointed out that the present thermodynamic model is based on the interpolation of the thermodynamic models of the binary edges systems without introducing the ternary parameter. Hence, the accuracy of the present calculations cannot be strongly supported. However, all the invariant reactions are located in the vicinity of the binary As-Fe and As-In edges where the ternary parameter is not effective and

Table 4 Calculated invariant reactions. The reaction type and temperature are shown in 1st and 2nd columns, respectively. The 3rd column indicates a symbol used to indicate the invariant reaction point in Figs. 2 and 3. The liquid compositions at the reaction point are specified in the last two columns.

Reaction	Temperature (K)	Symbol	Liquid compositions	
			x_{In}	x_{Fe}
$L \leftrightarrow L + \text{AsFe}$	1296	m_1	0.026	0.476
$L \leftrightarrow L + \text{AsFe}$	1294	m_2	0.465	0.035
$L \leftrightarrow L + \text{As}_2\text{Fe}$	1280	m_3	0.111	0.173
$L_1 \leftrightarrow L_2 + \text{AsFe} + \text{As}_2\text{Fe}$	1269	M_1	0.030	0.381
		M_1'	0.272	0.073
$L_1 + \text{AsFe} \leftrightarrow L_2 + \text{AsFe}_2$	1228	U_1	0.016	0.586
		U_1'	0.747	0.011
$L \leftrightarrow \text{AsFe} + \text{InAs}$	1205	m_4	0.485	0.015
$L + \text{AsFe} \leftrightarrow \text{As}_2\text{Fe} + \text{InAs}$	1203	U_2	0.435	0.018
$L \leftrightarrow L + \text{AsFe}_2$	1175	m_5	0.011	0.656
$L_1 \leftrightarrow L_2 + \text{As}_2\text{Fe}_3 + \text{AsFe}_2$	1174	M_2	0.011	0.646
		M_2'	0.881	0.006
$L_1 \leftrightarrow L_2 + (\delta\text{Fe}) + \text{AsFe}_2$	1117	M_3	0.008	0.745
		M_3'	0.983	0.006
$L + \text{As}_2\text{Fe}_3 \leftrightarrow \text{AsFe} + \text{AsFe}_2$	1095	U_4	0.878	0.003
$L \leftrightarrow \text{As}_2\text{Fe} + \alpha\text{As} + \text{InAs}$	1004	E_1	0.141	0.002
$L + \text{AsFe} \leftrightarrow \text{InAs} + \text{AsFe}_2$	717	U_5	0.993	$<1 \times 10^{-5}$

Fig. 3 Enlargement of the monovariant lines in (a) As-rich region, (b) In-rich region and (c) As-Fe binary edges region. The primary crystallizing phase field is indicated in each figure.

the phase equilibria are entirely determined by the thermodynamic state of the binary edge system. The present thermodynamic models for each binary system are considered to be well established based on the reliable experimental

data and the first-principles total energy calculations of the formation energies of the compounds. Hence, it is considered that the present result for liquidus surface and invariant reactions should be tentative but close to the reality.

Fig. 4 Vertical section at $x_{\text{As}} = 0.5$ between AsFe and InAs compounds.

As already mentioned in the introduction, the optimization of the fabrication process parameters for spin injection device has been currently attempted by a trial and error. It is generally considered that growth process of Fe on semiconductor in relatively high temperature range (420–450 K) does not suffer from the formation of defects in the Fe film. However, the recent work showed that the epitaxial growth of Fe films on the InAs substrate at 450 K involves the interface reaction, resulting in the formation of a compound at the interface.⁷⁾ On the other hand, the fabrication process at 296 K leads to a clear interface, i.e., the interface without the formation of compound.⁷⁾ The critical temperature at which the reaction occurs at the Fe/InAs interface has not been clarified. The calculated isothermal section at 300 K is shown in Fig. 5(a). It is noted that at this temperature, the energy of the formation of the compounds plays a dominant role in determining the phase equilibria. The accuracy for InAs, AsFe and AsFe₂ are well supported by the experimental data and the first-principles calculations.^{14,15)} At this temperature, the InAs compound is in equilibrium with the As₂Fe, AsFe and AsFe₂, while (α Fe) is not stable in contact with the InAs, which is consistent with the one obtained from the Miedema's estimation of the formation energy of compound.¹²⁾ Though the identification of the types of the compounds formed at the Fe/InAs interface requires the diffusion path between Fe/InAs diffusion couples to be investigated in detail, the reaction is expected not to proceed substantially at this low temperature.

The isothermal section at 450 K is shown in Fig. 5(b). It is noticed that the Fe/InAs contact is not directly in equilibrium and its hybrid structure involves a reaction at this temperature. It is important to note that the liquid phase exists in the AsFe + InAs + L₂, AsFe₂ + InAs + L₂ three phase regions, (α Fe) + L₂ two phase region at 450 K. As pointed out by Beyers *et al.*,⁹⁾ if the liquid phase exists during the growth process of thin film layer on the semiconductor, melting and the re-solidification of the metallization layer occur at the interface. The isothermal section shown in Fig. 5(b) indicates that the liquid phase in the fabrication process at 450 K may lead to the formation of AsFe₂ compound. The present calculation demonstrated that the liquid phase appear at 429.8 K through a degenerated reaction in the As-In binary edge system. Hence, the fabrication at the temperature lower than 429.8 K can prevent the reaction

Fig. 5 Calculated isothermal sections at (a) $T = 300$ K and (b) $T = 450$ K.

associated with the liquid phase. Although we cannot readily conclude that the reaction at the interface observed at 450 K⁷⁾ is associated with the existence of the liquid phase, the present thermodynamic calculations suggest the growth temperature lower than 429.8 K.

4. Conclusion

In this study, we performed the thermodynamic modeling of the As-Fe-In system based on CALPHAD approach. First we presented the thermodynamic modeling of the Fe-In binary edge system. Then, by utilizing the models for As-In¹⁵⁾ and As-Fe¹⁴⁾ systems, the liquidus surface and the invariant reactions were calculated. The special attention was directed to the isothermal sections at 300 K and 450 K, which are critically relevant to the fabrication process of Fe/InAs hybrid structure. The present calculated results are quite suggestive of the possibility that the liquid phase exists at the interface between Fe film and InAs substrate during the fabrication process at 450 K, which leads to the formation of AsFe₂ compound. The fabrication at the temperature lower than 429.8 K can prevent the reaction associated with the liquid phase. The present thermodynamic calculations can be utilized to optimize the fabrication process parameters for Fe/InAs hybrid structure.

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