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Thermal analysis and thermodynamic prediction of phase equilibria in the ternary Au–Ga–Sb system

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ABSTRACT

Phase transition temperatures of the selected samples with compositions along isopleths: GaSb–$AuGa_2$, GaSb–AuGa, Au–GaSb, Sb–AuGa, GaSb–$Au_{0.3333}Sb_{0.6667}$ and Ga–$Au_{0.5}Sb_{0.5}$ were measured using differential scanning calorimetry (DSC). Experimentally determined phase transition temperatures were compared with the results of thermodynamic calculation. Also, predicted phase equilibria at room temperature were compared with the literature experimental data.

1. Introduction

GaSb-based semiconductor alloys have emerged as critical materials for infrared lasers, thermophotovoltaic devices, solar cells, and transistors [1,2]. Since processing of semiconductor devices normally includes exposure to elevated temperatures, interface reactions often occur during the metallization step and further heat treatments [3]. In order to understand these reactions, a thorough knowledge of the phase diagrams of ternary systems including transition metals under consideration with elements of group III and V is essential. However, experimentally determined ternary phase diagrams are available only for the limited number of Ga–Sb-based ternary systems [3–6].

One among important, but not sufficiently known, systems is the ternary Au–Ga–Sb system. In this study, phase transition temperatures of the samples along six vertical sections were determined using differential scanning calorimetry (DSC), as a contribution to the better knowledge of the Au–Ga–Sb system phase equilibria. The literature thermodynamic descriptions of the constitutive binaries were used for thermodynamic prediction of the investigated vertical sections. Calculated phase diagrams were compared with the DSC results from this study and good mutual agreement was noticed.

2. Literature review

There are numerous references [7–17] regarding thermodynamics, phase equilibria and crystallography of the constitutive binary systems Au–Ga, Au–Sb and Ga–Sb. Detailed review of this literature data can be found in the Landolt-Börnstein Database—for the Au–Ga system [7], for the Au–Sb system [8,9], and for the Ga–Sb [10,11]). Thermodynamic optimization of the Au–Ga system has been done recently by Wang et al. [12]. Thermodynamic assessment of the Au–Sb system was done by Chevalier [13], followed by Kim et al. [14]. The latest experimental investigation and thermodynamic assessment of that system was carried out by Zoro et al. [15] within the framework of the COST 531 project [16]. The Ga–Sb system was assessed by Ansara et al. [17].

Limited information is available regarding the phase equilibria in the ternary Au–Ga–Sb system. Its phase diagram was partially experimentally investigated by Tsai and Williams [18] using X-ray powder diffraction, and phase equilibria at the room temperature was determined. These results indicated that both AuGa and $AuGa_2$ compounds were in the thermodynamic equilibrium with GaSb. Later on, Liu and Mohney [19] investigated condensed phase equilibria in many important transition metal–Ga–Sb systems

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and performed thermodynamic calculation to determine isothermal section of the Au–Ga–Sb ternary system at 298 K, which was in good agreement with the results of Tsai and Williams [18].

3. Experimental

The alloy samples were prepared by melting the pieces of the constituent pure metals—antimony (99.99 mass%), gold (99.99 mass%) and gallium (99.9999 mass%), under argon atmosphere in alumina crucibles using induction furnace. The alloys were melted and cooled repeatedly to ensure compositional homogeneity. The samples' masses were about 1 g. The total mass losses of prepared samples were less than 0.5 mass%, so the nominal compositions of the alloys were accepted for further investigation.

The phase transformation temperatures were determined by DSC method. The measurements were performed on a SDT Q600 (TA instruments), under flowing argon atmosphere, using alumina crucibles, the heating rate 5 °C/min, and were repeated 3 times for each composition. Before the measurements, temperature calibration of DSC was performed under the experimental conditions, using Au (99.99 mass%), Sb (99.99 mass%), Sn (99.99 mass%) and In (99.999 mass%).

4. Thermodynamic calculation of the Au–Ga–Sb phase diagram

The phase diagram of the Au–Ga–Sb system was calculated using CALPHAD method [20], based on published thermodynamic descriptions of the constitutive binary systems.

The thermodynamic parameters for the Au–Ga, Au–Sb and Ga–Sb systems were taken from the papers of Wang et al. [12], Zoro et al. [15] and Ansara et al. [17], respectively. The Gibbs energy functions for pure elements are based on the Scientific Group Thermodata Europe (SGTE) database values [21], except for the Au and Ga—in the high temperature solution phase D024 (α) from the Au–Ga binary system, not presented in the SGTE database, but specified in Ref. [12].

There are 12 phases in the ternary Au–Ga–Sb system. Their common names, thermodynamic database names and crystallographic data are given in Table 1.

The binary thermodynamic parameters, taken from literature and used for prediction of phase equilibria in the Au–Ga–Sb system, are listed in Table 2. The ORTHORHOMBIC_GA and RHOMBO_A7 phases were treated as pure components.

Phase diagrams of the constitutive binaries, calculated using thermodynamic dataset from Table 2, are shown in Fig. 1. Fig. 1a represents calculated phase diagram of the Au–Ga binary system.

Table 1
Considered phases and their crystallographic data [12,22].

Phase	Thermodynamic database name	Pearson symbol	Space group
Liquid	LIQUID		
(Au)	FCC A1	*cF4*	$Fm\bar{3}m$
α	D024	*hP16*	$P63/mmc$
β	AU7GA2_H	(a)	…
β′	AU7GA2_L	(b)	…
γ	AU7GA3	(b)	
AuGa	AUGA	*oP8*	*Pnma*
$AuGa_2$	AUGA2	*cF12*	$Fm\bar{3}m$
(Ga)	ORTHORHOMBIC_GA	*oC8*	*Cmca*
$AuSb_2$	AUSB2	*cP12*	*Pa3*
(Sb)	RHOMBO_A7	*hR2*	$R\bar{3}m$
GaSb	ZINCBLENDE_B3	*cF8*	$F4\bar{3}m$

(a) *Hexagonal*; (b) *Orthorhombic*.

Table 2
The optimized binary parameters used in this study.

Phase and thermodynamic model	Thermodynamic parameter	Ref.
LIQUID (Au,Ga,Sb)	${}^0L^{LIQUID}_{Au,Ga} = -71830.123+42.286T-4.289T\ln T$	[12]
	${}^1L^{LIQUID}_{Au,Ga} = -22892.323+5.069T$	[12]
	${}^2L^{LIQUID}_{Au,Ga} = -8839.911+7.674T$	[12]
	${}^0L^{LIQUID}_{Au,Sb} = -10288.0428-14.7865028T$	[15]
	${}^1L^{LIQUID}_{Au,Sb} = -2901.66787-7.2503632T$	[15]
	${}^2L^{LIQUID}_{Au,Sb} = 1217.43604-4.74909763T$	[15]
	${}^0L^{LIQUID}_{Ga,Sb} = -13953.8+71.0787T-9.6232T\log T$	[17]
	${}^1L^{LIQUID}_{Ga,Sb} = 1722.9-1.92588T$	[17]
	${}^2L^{LIQUID}_{Ga,Sb} = 2128.3$	[17]
FCC_A1 $(Au,Ga,Sb)_1(Va)_1$	${}^0L^{FCC\_A1}_{Au,Ga:Va} = -31511.768-12.788T$	[12]
	${}^1L^{FCC\_A1}_{Au,Ga:Va} = -20073.352+14.067T$	[12]
	${}^0L^{FCC\_A1}_{Au,Sb:Va} = 31456.5511-35.1097911T$	[15]
D024 $(Au,Ga)_1$	${}^0L^{D024}_{Au,Ga} = -41291.692-0.227T$	[12]
	${}^1L^{D024}_{Au,Ga} = -15367.206-3.768T$	[12]
AU7GA2_H $(Au)_{0.7895}(Ga)_{0.2105}$	${}^0G^{Au7Ga2\_H}_{Au:Ga} = -11148.550-1.257T+0.7895GHSERAU+0.2105GHSERGA$	[12]
AU7GA2_L $(Au)_{0.7777}(Ga)_{0.2223}$	${}^0G^{Au7Ga2\_L}_{Au:Ga} = -12640.544+0.326T+0.7777GHSERAU+0.2223GHSERGA$	[12]
AU7GA3 $(Au)_{0.7}(Ga)_{0.3}$	${}^0G^{Au7Ga3}_{Au:Ga} = -16720.107+2.397T+0.7GHSERAU+0.3GHSERGA$	[12]
AUGA $(Au)_{0.5}(Ga)_{0.5}$	${}^0G^{AuGa}_{Au:Ga} = -24002.418+4.422T+0.5GHSERAU+0.5GHSERGA$	[12]
AUGA2 $(Au)_{0.333333}(Ga)_{0.666667}$	${}^0G^{AuGa2}_{Au:Ga} = -24823.663+5.961T+0.333333GHSERAU+0.666667GHSERGA$	[12]
ZINCBLENDE_B3 $(Ga)_{0.5}(Sb)_{0.5}$	${}^0G^{ZINCBLENDE\_B3}_{Ga:Sb} = -21738.1-10.53764T+2.692876T\log T-0.001377917T^2+0.5GHSERGA+0.5GHSERSB$	[17]
AUSB2 $(Au)_{0.333333}(Sb)_{0.666667}$	${}^0G^{AuSb2}_{Au:Sb} = -5721.66949+6.93505837T+0.333333GHSERAU+0.666667GHSERSB$	[15]

It consists of liquid phase, three solid solution phases: fcc (Au), hcp (D024) and orthorhombic (Ga), and five intermetallic compounds: β-Au7Ga2_H, β′-Au7Ga2_L, γ-Au7Ga3, AuGa and AuGa2, which were treated as stoichiometric compounds. Fig. 1b shows calculated phase diagram of the Au–Sb binary system. Beside the liquid phase, fcc (Au) and rhombohedral (Sb) solid solution phases, $AuSb_2$ intermetallic compound, with narrow homogeneity range, is present. Calculated phase diagram of the Ga–Sb system (Fig.1c) includes one stoichiometric intermetallic compound GaSb.

5. Results and discussion

There is a small amount of experimental information regarding the phase equilibria and thermodynamics of the Au–Ga–Sb ternary system. No phase equilibria data, except those given in Ref. [18], and no thermodynamic data are available for determination of ternary parameters. So, thermodynamic calculations of phase equilibria in this system were done only on the basis of binary thermodynamic data. Predicted results were compared with experimental results from this study and literature [18].

Due to the fact that there is still no complete data to give a full overview on thermodynamic behavior and phase equilibria of the