Phase equilibria in the In–Sb–Bi system at 300 °C

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Abstract: Binary thermodynamic data, successfully used for phase diagram calculations of the binary systems In–Sb, Bi–Sb and In–Bi, were used for the prediction of phase equilibria in the ternary system In–Sb–Bi at 300 °C. The predicted equilibria were compared with the results of SEM–EDX analysis.

Keywords: In–Sb–Bi system, phase diagram, thermodynamics.

INTRODUCTION

InSb and GaSb are two examples of so-called narrow band gap semiconductors with high electron mobility. They have gained increasing interest within the last decade,1,2 because of their high potential for a number of electronic and optoelectronic applications.

Knowledge of the phase equilibria in ternary systems of the corresponding metals with the elements of III–V semiconductor compounds is an important step toward a better understanding of contact formation and presents a basis for the development of new and improved contact materials. The aim of this study was to calculate the phase equilibria of the In–Sb–Bi system at 300 °C according to the CALPHAD approach3–5 and to compare the obtained results with experimental results based on SEM–EDX analysis.

THERMODYNAMIC MODELLING

Pure elements

The pure solid elements at 298.15 K and 1 bar in their stable form were chosen as the reference state for the systems (SER). Version 4.4 of the SGTE Unary Database (Scientific Group Thermodata Europe) of phase stabilities for stable and metastable states of the pure elements6 was used.
Binary systems

The thermodynamic descriptions of the binary alloys, were taken from the literature, i.e., for the In–Sb system,\(^7\) for the Bi–Sb system\(^8\) and the In–Bi system.\(^9\)

Liquid and solid solution phases

The Gibbs energies of liquid and solid phases are described by the sub-regular solution model with the Redlich–Kister polynomial as follows:

\[
G^m = \sum_{x=0}^{m} L^m A_B (x_A - x_B)^m
\]

where \(L^m A_B\) is a temperature-dependent parameter optimized on the basis of the available thermodynamic and phase diagram data, and A, B are the elements of the system.

Stoichiometric compounds

The Gibbs energy of a compound, e.g., \(X_m Y_n\), is generally described as:

\[
G_{X_m Y_n} = \frac{m}{m+n} G_X + \frac{n}{m+n} G_Y + \Delta G_{X_m Y_n}^f
\]

where \(\Delta G_{X_m Y_n}^f\) represents the Gibbs energy of formation per mole of atoms of the \(X_m Y_n\) compounds and is expressed by the following equation:

\[
\Delta G_{X_m Y_n}^f = A + BT
\]

The In–Sb–Bi ternary system

There is still no complete data to give a full overview on the thermodynamic behavior and phase equilibria of the mentioned ternary system. Therefore, some new results of an investigation of the phase equilibria of In–Sb–Bi system are presented in this contribution.

EXPERIMENTAL

Alloys of the In–Sb–Bi system were prepared from pure metals (99.99 \%) by induction melting of weighed amounts of indium, antimony and bismuth under an argon atmosphere.

After melting, the alloys were subjected to homogenizing annealing in evacuated quartz glass capsules. The annealing was done in a resistance furnace at 300 °C for 100 h with subsequent quenching into ice water.

The equilibrium compositions of samples were determined using a JEOL scanning electron microscope with an accelerating voltage of 20 kV and EDX analyzer.

RESULTS AND DISCUSSION

The values of integral molar Gibbs excess energies, \(G_{ij}^{E}\), for the constitutive binary systems In–Sb,\(^7\) Bi–Sb\(^8\) and In–Bi\(^9\) were used as the starting binary thermo-
dynamic data for the calculation. All these data are included in the COST 531 binary database.\textsuperscript{10}

The optimized Gibbs energy of the intermediate phase InSb was given as:\textsuperscript{7}
\[ G(ZINCBLENDE\_B3,IN:SB;0) = 0.5\*GHSERIN + 0.5\*GHSERSB – 15849.3 + 0.293139\*T + 1.293581\*T\*LN(T) \quad (298.14<T<3000.00) \]

The Gibbs energies for BiIn, BiIn\(_2\) and Bi\(_3\)In\(_5\) were given as:\textsuperscript{9}
\[ G(BI1IN1,BI:IN;0) = –732.2–3.7906 \* T + 0.5\*GHSERBI + 0.5\*GHSERIN \quad (298.14<T<3000.00) \]
\[ G(BI1IN2,BI:IN;0) = –481.1–4.188\*T + 0.333333\*GHSERBI + 0.666667\*GHSERIN \quad (298.14<T<3000.00) \]
\[ G(BI3IN5,BI:IN;0) = –544–4.12287\*T + 0.375\*GHSERBI + 0.625\*GHSERIN \quad (298.14<T<3000.00) \]

The optimized thermodynamic parameters for the LIQUID, TETRAGONAL\(_A6\), RHOMBOHEDRAL\(_A7\) and BIIN\_EPSILON phases used for the calculation are given in Table I.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Bi–In\textsuperscript{9}</th>
<th>In–Sb\textsuperscript{7}</th>
<th>Bi–Sb\textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIQUID</td>
<td>( ^0 L_{A,B} )</td>
<td>-7165.0–0.3754*T –25631.2+102.9321*T –13.45815*T*LN(T)</td>
<td>2230+0.06*T</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^1 L_{A,B} )</td>
<td>1503.8–0.5418*T –2115.4–1.31907*T</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^2 L_{A,B} )</td>
<td>1221.15–1.65967*T +2908.9</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^3 L_{A,B} )</td>
<td>-1627+2.764*T</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>TETRAGONAL(_A6)</td>
<td>( ^0 L_{A,B} )</td>
<td>5646.8–26.868*T</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RHOMBOHEDRAL(_A7)</td>
<td>( ^0 L_{A,B} )</td>
<td>22500</td>
<td>15*T</td>
<td>10150–6.30*T</td>
</tr>
<tr>
<td></td>
<td>( ^1 L_{A,B} )</td>
<td>–</td>
<td>–</td>
<td>150</td>
</tr>
<tr>
<td>BIIN_EPSILON</td>
<td>( ^0 L_{A,B} )</td>
<td>4904.5–28.9743*T</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>( ^1 L_{A,B} )</td>
<td>-1386.4</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The phase diagram of the isothermal section at 300 °C, shown in Fig. 1, was calculated only on the basis of the binary thermodynamic data using the Redlich–Kister–Muggianu model for ternary thermodynamic functions. The calculation was performed using Thermo-Calc software (TC4A version).

The predicted isothermal section of the In–Sb–Bi ternary system at 300 °C includes one three-phase region (InSb + Rhombo + Liquid), three two-phase regions (InSb + Rhombo; InSb + Liquid; Rhombo + Liquid) and one single-phase region (Liquid).

The SEM (scanning electron microprobe) with EDX (energy dispersive X-ray) analysis can give very important information of the composition of the searched phases. Reasonable agreement between the experimental data and the binary-based prediction was found. All the results from the SEM analysis are given in Table II.
TABLE II. Results of the SEM – EDX analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Overall experimental composition/% at.</th>
<th>Theoretic. predicted phases</th>
<th>Experiment. determined phases</th>
<th>Exp. compositions of phases/% at.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(41.2 ± 1.8) % In</td>
<td>InSb</td>
<td>InSb</td>
<td>(51.1 ± 0.2) (48.7 ± 0.3) (0.2 ± 0.3)</td>
</tr>
<tr>
<td></td>
<td>(19.7 ± 1.4) % Sb</td>
<td>Liquid</td>
<td>Liquid</td>
<td>(33.5 ± 1.6) (1.2 ± 0.9) (65.3 ± 1.2)</td>
</tr>
<tr>
<td></td>
<td>(39.1 ± 1.5) % Bi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(31.4 ± 1.1) % In</td>
<td>Rhombo</td>
<td>Rhombo</td>
<td>(1.1 ± 0.3) (36.1 ± 1.5) (62.8 ± 1.5)</td>
</tr>
<tr>
<td></td>
<td>(37.6 ± 1.2) % Sb</td>
<td>InSb</td>
<td>InSb</td>
<td>(50.5 ± 0.3) (49.5 ± 0.3)</td>
</tr>
<tr>
<td></td>
<td>(31.0 ± 0.9) % Bi</td>
<td>Liquid</td>
<td>Liquid</td>
<td>(5.4 ± 0.3) (7.3 ± 0.4) (87.3 ± 0.3)</td>
</tr>
<tr>
<td>3</td>
<td>(17.1 ± 0.7) % In</td>
<td>Rhombo</td>
<td>Rhombo</td>
<td>(1.0 ± 0.6) (83.6 ± 0.6) (15.4 ± 0.6)</td>
</tr>
<tr>
<td></td>
<td>(68.0 ± 1.1) Sb</td>
<td>InSb</td>
<td>InSb</td>
<td>(51.1 ± 0.2) (48.9 ± 0.2)</td>
</tr>
<tr>
<td></td>
<td>(14.9 ± 0.7) % Bi</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Results of SEM analysis, comparison with the prediction at 300 ºC. Full symbols – overall composition, empty symbols – compositions of the phases (see Table II).

Fig. 2. In31Sb38Bi31 sample: Characteristic SEM photograph (InSb-dark phase; Rhombo-gray phase; Liquid-light phase).
CONCLUSION

A binary-based, thermodynamic prediction of the equilibria of the In–Sb–Bi system was performed using optimized thermodynamic parameters for the constituent binaries taken from the literature. The estimated phase diagram at 300 ºC was compared with the experimental results obtained by SEM analysis. The experimentally determined liquid and rhombo phases for the In0.31Sb0.38Sn0.31 sample contained higher contents of bismuth compared to the prediction, which suggests the need for the introduction of ternary interaction parameters for the rhombo and liquid phase. In addition to the experimental results presented in this work, more thermodynamic and phase equilibrium data at various temperatures are required for a detailed assessment.

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REFERENCES

3. www.calphad.org
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