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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Interaction of Metals with III–VI Semiconductors

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Abstract—An analysis of experimental data and thermodynamic calculations shows that the Gibbs free energy versus temperature relationship can serve as a reliable basis for the prediction of the occurrence or absence of exchange chemical reactions between gallium, indium, and thallium monochalcogenides, with allowance for the character of interaction of the components in the boundary binaries of the particular ternary system.

Chalcogenides of Group IIIA elements have many valuable properties that render them promising semiconductors: they have considerable conductivities, small current carrier mobilities, high thermopowers, and low thermal conductivities; they are sputtered without decomposition and retain semiconductor conductivity trends in the liquid state [1]. Therefore, these chalcogenides are promising semiconductors. While operating, a working semiconductor element is always in contact with current-carrying metal units; at the contact spot, various physicochemical interactions can occur to form eutectics, solid solutions, or new phases [2–4]. The nascent compounds can differ in properties from both the semiconductor and the metal, causing pore formation and cracking in the contact area.

The selection of commutation materials that would be chemically inert toward the semiconductor and provide stable performance is a challenging problem in semiconductor engineering. To make the selection, the engineer should understand the character of the interaction of semiconductors with various metals.

The purpose of this work was to summarize and analyze literature data on interaction of metals with gallium, indium, and thallium monochalcogenides. The literature data are compared with the results of calculation of the Gibbs free energy ΔG_T for the displacement reactions

$$A^{III}B^{VI} + xM \longrightarrow M_xB^{VI} + A^{III}.$$

The table compiles all experimental data available on the character of physicochemical interaction of gallium, indium, and thallium with metals; they are labeled with asterisks. The table also includes our predictions of exchange interaction based on our computations of the Gibbs free energy by using the procedure in [5].

Compounds included in the thermodynamic calculations are specified in the table. For In, Ge, Sn, Fe, and Ni, the Gibbs free energies of exchange reactions were calculated with allowance for the formation of In_2X_3, GeX_2, SnX_2, FeX_2, and NiX_2, respectively. Identical values were obtained with allowance for the formation of InX, GeX, SnX, FeX, and NiX, respectively (see table).

The experimental evidence in the table shows that GaS enters into chemical reactions with Sn [6]; GaSe, with Tl [12] and Yb [13]; GaTe, with Yb [23]; InS, with Cd [32]; InSe, with Yb [34] and Sb [38]; InTe, with Ho [40] and, possibly, with Sb [43] (according to [41, 42], the InTe–Sb system is quasi-binary); and TlSe, with Sb [49, 50]. The other of the experimentally studied $A^{III}B^{VI}$–M systems are quasi-binary.

The Gibbs free energies were calculated for all of the $A^{III}B^{VI}$–M systems studied, except for thallium monochalcogenide systems (their thermodynamic properties have not been determined adequately) and systems containing ytterbium. Although only one of the six gallium and indium monochalcogenide systems of the type $A^{III}B^{VI}$–M had been studied experimentally, we calculated exchange interactions for all six of the systems. Having done this, we are able to predict the character of physicochemical interaction in systems of this type.

Up to now, 35 of the $A^{III}B^{VI}$–M systems have been studied. For 29 out of the 35 systems studied, experimental data can be compared with thermodynamic calculations. For 5 out of these 29 (which constitutes approximately 17%, as for $A^{IV}B^{VI}$–M systems [5]), simulations are inconsistent with experiment (table). For the InTe–Sb system, experimental data are at variance: Gregory [43] suggests that antimony reacts chemically with InTe to form InSb, whereas Bobrov *et al.* [41] and Dashevskii *et al.* [42] report that the InTe–Sb systems is quasi-binary. In this case, thermo-

Character of interaction in $A^{III}B^{VI}$–M mixtures

	Cd (CdX)	In (InX)	Tl	Sm (SmX)	Ho (HoX)	Yb	Ge (GeX)	Sn (SnX)
GaS	No	No		Yes Yes* [6]	Yes		No	No
GaSe	No	No No* [11]	Yes* [12]	Yes	Yes	Yes* [13]	No No* [14, 15]	No No* [16]
GaTe	No	No		Yes	Yes	Yes* [23]	No No* [24–26]	No
InS	Yes Yes* [32]	–		Yes	Yes		No No* [33]	No
InSe	Yes	–		Yes		Yes* [34]	No No* [35]	No No* [16, 36]
InTe	Yes	–		Yes	Yes Yes* [40]		No	No
TlS								
TlSe							No* [48]	

	Pb (PbX)	Sb (Sb_2X_3)	Bi (Bi_2X_3)	Mn (MnX)	Fe (FeX)	Co (CoX_2)	Ni (NiX)
GaS	No No* [7]	No No* [8]	No No* [9]	Yes No* [10]	No	No	No
GaSe	No No* [17, 18]	No No* [19, 20]	No No* [21, 22]	Yes	No	No	No
GaTe	No	No	No No* [27, 28]	No/Yes No* [29]	No No* [30]	No No* [31]	No No* [31]
InS	No	No	No	Yes	No	No	No
InSe	No No* [37]	No Yes* [38]	No	Yes No* [39]	No	No	No
InTe	No	No No* [41, 42] Yes* [43]	No No* [44, 45]	Yes No* [46]	No No* [47]	No	No
TlS							
TlSe		Yes* [49, 50]					

Note: Yes means that a reaction occurs; No, that no reaction occurs; and No/Yes, that a reaction does not occur at low temperatures and does occur at high temperatures. An asterisk means that experimental evidence is available. The compounds included in thermodynamic calculations are parenthesized.

dynamic data do agree with experimental data of one work and do not with the other. Discordance is also observed for the InSe–Sb system: according to Ragimova *et al.* [38], Sb reacts with InSe with the formation of InSb and In_2Se_3. The inclusion of indium antimonide into the calculation scheme can possibly help removing this discordance.

The other three cases of disagreement between the calculation and experiment are $A^{III}B^{VI}$–Mn systems: calculations indicate exchange chemical reactions for all systems except the GaTe–In system (in which the components do not react at low temperatures); experimental evidence suggests that all of these systems are quasi-binary. These discrepancies can arise from either of the following reasons: insufficient accuracy with which the thermodynamic properties of manganese chalcogenides were determined; measurement errors in experimental studies of $A^{III}B^{VI}$–Mn systems; and kinetic hindrances, which render the rates of exchange reactions negligibly low, so that a metastable phase diagram is constructed.

Thus, we have compared experimental data on the character of physicochemical interaction between gallium and indium monochalcogenides and metals and the results of thermodynamic calculations. As was the case with $A^{II}B^{VI}$–M and $A^{IV}B^{VI}$–M systems [5, 51], the

occurrence or absence of chemical reactions in a particular system is predicted fairly reliably by simulations of temperature variations of the Gibbs free energy of exchange reactions for $A^{III}B^{VI}$–M systems. The prediction will be more reliable if the thermodynamic analysis is complemented by an analysis of phase diagrams of the boundary binaries of every ternary system and the stabilities of all existing binary phases are accounted for.

Thus, the occurrence or absence of exchange chemical reactions for gallium, indium, and thallium monochalcogenides can reliably be predicted based on temperature variations of the Gibbs free energy with allowance for the character of interaction of the components of the boundary binaries of a ternary system.

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