

Estimation of activity data for the Ga-Sb, Ga-S and Sb-S systems regarding the doped GaSb semiconductor crystals

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Abstract: GaSb based materials have been the subject of increasing attention in current semiconductor production. We report the preparation of single crystals grown by the Czochralski technique without encapsulant in a flowing variously doped hydrogen atmosphere. Consequently the Ga-Sb-S system has become important accounting for sulphur doping which requested thermodynamic evaluations based on the minimization of Gibbs energy and/or on the prediction method calculating respective activities from the phase diagram. Beside a survey character of this paper, the actual activity estimation for binaries in question are presented showing a rather high scatter of both published and calculated data.

INTRODUCTION: GaSb BASED SEMICONDUCTORS

Gallium antimonide (GaSb) based crystals (1-3) are a direct band gap material of interest for the production of various semiconductor devices such as low threshold Gunn oscillators, low noise APDs (4), LEDs and LDSs (5) and high speed electronic devices (6). GaSb has a gap of 0.72 eV at room temperature and a cubic lattice constant of 6.096 Å which is appreciably larger than that for what has so far been the most convenient semiconductor GaAs (5.654 Å) and a little greater than that for InAs (6.058 Å). Since InSb is about 6.479 Å the addition of about 10% Sb results in a lattice match to GaSb as well as the Sb- and As- doped $\text{Al}_{0.4}\text{Ga}_{0.6}$. Undoped bulk-grown GaSb crystals are p-type (1) with a hole concentration of the order of 10^{16} cm^{-3} . The native defects responsible are Ga at the Sb sites. It was also suggested that a Ga-vacancy can be accompanied with a $\text{Ga} \Rightarrow \text{Sb}$ substitution. The electron mobility, however, is about $5 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 10^{17} cm^{-3} doping in bulk GaSb at room temperature which is comparable to that of GaAs, while the hole mobilities of about $5 \times 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ match that of GaAs at 10^{16} cm^{-3} doping. Donor dopants are S, Se and Te with the depth of shallow levels decreasing from 60 meV to 40 meV, respectively. We have successfully studied (7,8) the deep metastable centres (conventionally called the DX centres (9)) employing the Czochralski grown GaSb single crystals doped with S and Te. The need to overcome many difficulties to achieve a suitable procedure for the preparation of good quality single crystals focused our interest on some aspects of composition and growth thermodynamics.

CRYSTAL GROWTH AND PREVIOUS DATA TREATMENTS

GaSb has a melting point of 712 °C, which is substantially lower than the 1240 °C of GaAs. Sb loss at moderate temperatures and the formation of surface scum (2) by gallium oxides are often cited as processing problems. On the other hand, the material is stable against oxidation by water vapour in contrast to Al-Ga-Sb compounds with high Al contents. The growth of S-doped GaSb has been reported earlier (10-13). The behaviour of sulphur during the growth was mainly explained by its evaporation from the melt, because it is known that its solubility is very low, viz. 7.2 ppm in the melt. Similarly a slight Sb excess is a useful feature in the standard growth conditions in order to compensate for Sb volatilization and help preserve the stoichiometry of the grown crystal. For a standard preparation of the GaSb single crystals (3,7,8,12) (grown by the Czochralski method without encapsulant in a hydrogen atmosphere) the S concentration (calculated from Hall measurements) reached a limited value of $1 \times 10^{17} \text{ atoms cm}^{-3}$ in the crystals despite the fact that the starting amount in the melt exceeded about $2 \times 10^{20} \text{ atoms cm}^{-3}$. It seems that evaporation begins at the 7.2 ppm level already mentioned (0.0043 at.%) (14)). The S concentrations, however, were from 0.0035 to 1.112 at.% (8) so that the limiting solubility was substantially exceeded, and the Ga_2S solid is thought to be created. Such a relatively high concentration of sulphur was intentionally taken into account during the mathematical evaluation to appreciate the behaviour of sulphur when it can no longer dissolve in the melt. As a result, higher mechanical stresses and tension were created on the solidification interface which consequently disturbed a single crystalline growth.

Table I. Literature values of the limiting activity coefficient ($\ln \gamma_S$) of sulphur in the Ga-S (average -13.4) and Sb-S (average -5.7) binary systems at temperatures of 985 K for the standard state of $S_{(1)}$

Ga-S	Sb-S	Remarks
-15.6	-6.6	from the phase diagram, selected in (18)
-16.76	-6.71	estimation on the basis of the empirical correlation in a row of Me-S systems (33)
-9.67	-3.52	estimation on the basis of a strictly regular solution model (Stringfellow (56))
-7.66		sulphur activity coefficient derived from EMF measurements (Fitzner (55))
	-9.97	from the phase diagram, estimated (55)
-17.65		phase diagram analysis (Rustamov <i>et al.</i> (57))
	-2.46	sulphur activity coefficient from equilibrium measurements (Twidwell (58))
	-4.99	sulphur activity from equilibrium measurements (Frohberg and Wang (59))

It became evident in the case of the S-Sb system and at these concentrations that sulphur exists in the form of a trisulphate below its melting temperature, i.e. sulphur is probably bound in the GaSb structure without creating any second phase. On the other hand Te forms two solid solutions with Sb from a concentration of about 3 at.% Te. The Te-S pseudobinary system shows the boundary line of solid solution at a S concentration of about 15 at%. At higher concentrations, therefore, Te-S solid solution appeared and no Te and S free atoms existed to form a second phase. It is necessary to add that if the Te concentration increased above 12 at% without exceeding that of sulphur, the calculated concentration of dopants was identical with that based upon measurements. However, when the S concentration exceeded 12 at% the calculated and measured concentrations were different irrespective of the Te concentration.

The chemical equilibrium in the Ga-Sb-S(-H) system was calculated using a general method based on minimization of the total Gibbs energy of the system on a set of points satisfying the material balance conditions (17). This was a modification of the White-Johnson-Dantzig (WJD) method based on earlier studies (19). The calculation program employed was the algorithm RAND described elsewhere (20) and applied in ref. (17) for twenty-eight chemical species. The model of a regular solution with a simple temperature-dependent interaction parameter was used. The behaviour of S in the melt was assumed to follow the Henry law. The limiting activity coefficient of sulphur depending on a composition of the melt was estimated on the basis of a regular solution model. The solid solution of Ga-Sb-S was assumed to be a pseudobinary solution of GaSb and S components (17). The activity coefficient of sulphur was estimated for the distribution coefficient of $k^{\circ}_{S(\text{GaSb})} = 0.06$ (17) as well as searched in the literature (Table I). The calculations were carried out at 985 K and atmospheric pressure to simulate the usual experimental conditions employed for crystal growth (12). Substantial differences in stoichiometry for the GaSb equilibrium liquid were established as a result of the Ga_2S solid formation and the starting amount of S effected the equilibrium amount of the individual phases and the distribution of sulphur between them (17). The maximum attainable S concentration in the single crystalline bowl was about 10^{17} atoms cm^{-3} (18). At higher values, the crystals became either polycrystalline or twinned. For this reason it seems that the second phase started to separate spontaneously from the melt, which resulted in the impaired single crystalline growth.

THERMODYNAMIC ANALYSIS BY PREDICTING METHOD

General

Calculation of activities from phase diagrams is one of several methods of obtaining data (21). The progress made is worth recapitulating. Initially, it was confined to a simple eutectic system (21, 22). This was later extended to diagrams containing intermetallic compounds. Chipman (23) used these formulae to calculate silicon activities in an iron-silicon alloy, though they are only applicable to compositions near a compound. Another method was used for the B_2O_3 -CaO system showing that a series of intermediate compounds as close to each other as possible were needed to obtain a more precise value. Further advances were made in 1964 by Y.S. Chou (24) (who suggested a method to calculate activity coefficients based on the Gibbs energy of a compound formation) and by Steiner *et al.* (25) showing a relatively good applicability under different known conditions. However, the former had some inherent integration difficulty while the latter required more information about the partial molar enthalpies of components and produced larger errors for the derivatives at phase boundary lines.

To overcome integration difficulties and extend the method to fit any type of compounds an approved method was suggested (26) on the basis of the Gibbs energy of formation as input data. For a phase diagram involving a series of intermediate compounds a method (22, 27) was proposed by K.C. Chou, where the temperature is employed as the integral variable and the formation entropy is used instead of other thermodynamic functions. Similarly the formula of melting point depression (22) was found useful in this binary system.

Calculation of Activities in the Binary Ga-Sb System

For a binary A-B system containing intermediate compound A_mB_n the standard Gibbs energy of formation reads as a sum of logarithms of mole fractions ($x_1^m x_2^n$) and activities ($\gamma_1^m \gamma_2^n$) of components A and B along the liquidus. Assuming that the temperature dependence of activity coefficients obeys a regular solution law, for a fixed temperature and after differentiation and rearrangement, we obtain:

$$d \ln (\gamma_1^m \gamma_2^n) = 1/RT_0 (-\Delta_f S^\circ dT - R (m \ln x_1 + n \ln x_2) dT - RT (m x_2 - n x_1) / (x_2 d \ln x_1)) \quad (1)$$

where $\Delta_f S^\circ$ denotes the entropy of formation of the A_nB_n compound. Using the Gibbs-Duhem equation it reads (26):

$$d \ln \gamma_1 = x_2 / (m - (m+n) x_1) d \ln (\gamma_1^m \gamma_2^n) \quad (2)$$

After the substitution of eq. 1 we obtain for component A:

$$d \ln \gamma_1 = -1 / (T_0 (m x_2 - n x_1)) (x_2 \Delta_f S^\circ / R + n (x_1 \ln x_1 + x_2 \ln x_2)) dT - d (T \ln x_1 / T_0) \quad (3)$$

similarly for component B making activity accessible upon integration. Phase diagrams for the binaries in question, ref. (28-33), are available from different sources (19), (cfr Fig. 1) including their thermodynamic properties (19, 33-44). No data have been reported on ternaries but it is clear that the solidus and liquidus temperatures must increase as experimentally illustrated in Fig. 2.

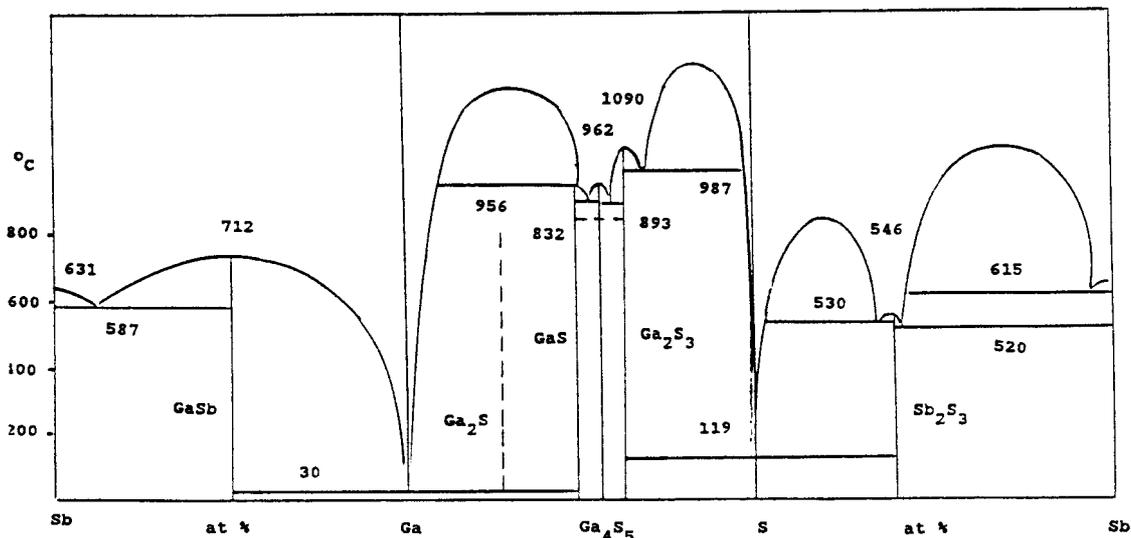


Fig. 1. Collective view to the binary edges of Ga-Sb-S system.

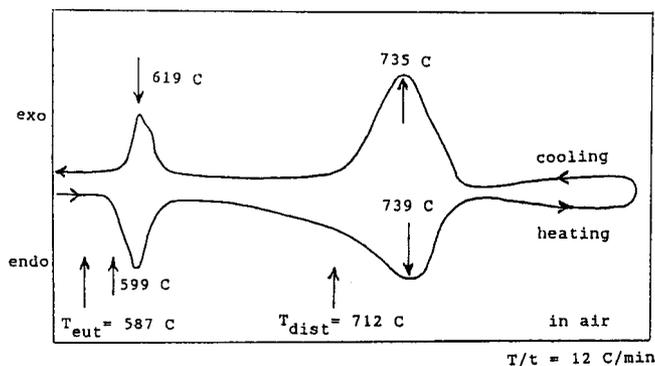


Fig. 2. DTA trace of GaSb single crystal saturated by sulphur dopant ($\leq 5\%$) showing the characteristic temperatures and their increase regarding the eutectic and dystectic temperatures for the (undoped) GaSb (compare Fig. 1).

Table II. Thermodynamic properties of Ga-Sb system calculated at 1000 K (G in $J \text{ mol}^{-1}$).

x_{Sb}	a_{Sb}	$G^{\text{ex}}_{\text{Sb}}$	a_{Ga}	$G^{\text{ex}}_{\text{Ga}}$	$\Delta G^{\text{ex}}_{\text{m}}$
0.1	0.046	-6476	0.913	119	-540
0.2	0.103	-5486	0.791	-99	-1176
0.3	0.169	-4773	0.671	-348	-1675
0.4	0.237	-4355	0.563	-526	-2057
0.5	0.38	-2280	0.389	-2098	-2193
0.6	0.522	-1164	0.247	-4012	-2304
0.7	0.664	-438	0.159	-5414	-1928
0.8	0.795	-55	0.093	-6357	-1316
0.9	0.896	-35	0.047	-6278	-658

Generally it was found difficult to obtain more precise in the Ga-Sb system at higher temperatures, mainly due to Sb volatility. Consequently, the experimental thermodynamic properties reported display sometimes poor agreeability while the comparable phase diagrams are of a relatively better quality and reliability. Therefore it was found convenient to apply the above method to the Ga-Sb system analysis assuming the existence of an intermediate compound GaSb. The input data (28) of the pure components ($\Delta_{\text{fus}}H^{\circ}(\text{Ga}) = 5590 \text{ J mol}^{-1}$ at 302.8 K and $\Delta_{\text{fus}}H^{\circ}(\text{Sb}) = 19874 \text{ J mol}^{-1}$ at 904 K) and that for the GaSb formation from the solid Ga and Sb compounds ($\Delta_f H^{\circ} = 42768 \text{ J mol}^{-1}$, $\Delta_f S^{\circ} = -12.836 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta C_p = 8.326 - 0.00728T \text{ J mol}^{-1} \text{ K}^{-1}$) as well as that for the liquid compounds ($\Delta_f H^{\circ} = -68233 \text{ J mol}^{-1}$ and $\Delta_f S^{\circ} = -55.304 \text{ J mol}^{-1} \text{ K}^{-1}$) yield the results listed in Table II (in the agreement with those ref. (27)).

Calculation Applicability in Analysing the Binary S-Sb and S-Ga Systems

The phase diagram of Sb-S system can be separated into two analogous binary subsystems S-Sb₂S₃ and Sb₂S₃-S. These phase diagrams belong to the group which involves two liquids α and β (and/or solid) coexisting phases where the predicting method is again applicable (45, 46). In particular we distinguish phase α on the left and phase β in the right hand side of the critical (apex) point of the immiscibility gap, cfr. Fig. 1, with the respective mole fraction and activity coefficients at a fixed temperature T_0 . Then

$$\phi_1^{\alpha} = - (x_2^{\alpha} \Sigma^{\alpha} - x_2^{\beta} \Sigma^{\beta}) / (x_2^{\beta} - x_2^{\alpha}) \quad (4)$$

where

$$\begin{aligned} \Sigma^{\alpha} &= x_1^{\alpha} \ln x_1^{\alpha} + x_2^{\alpha} \ln x_2^{\alpha} \\ \Sigma^{\beta} &= x_1^{\beta} \ln x_1^{\beta} + x_2^{\beta} \ln x_2^{\beta} \end{aligned} \quad (5)$$

According to Chou we can define (47)

$$\delta = T / (1 - T/\theta) \text{ and } \delta_0 = T_0 (1 - T_0/\theta) \quad (6)$$

where, according to the Richardson assumption (48), $\theta = \Delta_i H / \Delta S^{\text{ex}} = 3000$. The activity coefficient γ_i is then obtained

$$d \ln \gamma_1^{\alpha} = - \phi_1^{\alpha} d(\delta/\delta_0) - d(\delta \ln \delta_1^{\alpha}/\delta_0) \quad (7)$$

where γ_i^{α} and x_i^{α} represent values of activity coefficients and the mole fraction of components i in the α phases at the fixed temperature T_0 .

Table IIIa: Thermodynamic properties of S-Sb₂S₃ system calculated at 1073 K (G in J mol⁻¹).

$x_{\text{Sb}_2\text{S}_3}$	$a_{\text{Sb}_2\text{S}_3}$	a_{S}	$G^{\text{ex}}_{\text{Sb}_2\text{S}_3}$	G^{ex}_{S}	ΔG^{ex}
0.1	0.811	0.979	18762	751	2543
0.2	0.955	0.994	13947	1937	4339
0.3	0.983	0.995	10588	3137	5372
0.6	0.993	0.983	4494	8021	5905
0.7	0.989	0.955	3083	10330	5257
0.8	0.979	0.811	1801	12489	3939

Table IIIb: Thermodynamic properties of S-Sb₂S₃ system calculated 1223 K (G in J mol⁻¹).

x_{Sb}	a_{Sb}	$a_{\text{Sb}_2\text{S}_3}$	$G^{\text{ex}}_{\text{Sb}}$	$G^{\text{ex}}_{\text{Sb}_2\text{S}_3}$
0.1	0.969	0.985	23093	918
0.2	0.981	0.986	16170	2126
0.3	0.986	0.981	12099	3432
0.4	0.498	0.955	2228	4726
0.5	0.827	0.971	5117	6749
0.6	0.908	0.972	4213	9028
0.7	0.972	0.908	3338	11261
0.8	0.961	0.694	1864	12651
0.9	0.959	0.392	646	22987

Table IVa. Thermodynamic properties of the Ga - Sb system calculated at 1473 K.

x_{GaS}	a_{GaS}	a_{Ga}	$G^{\text{ex}}_{\text{GaS}}$	$G^{\text{ex}}_{\text{Ga}}$
0.1	0.402	0.959	17038	778
0.2	0.669	0.946	14787	2053
0.3	0.803	0.937	12058	3571
0.4	0.949	0.971	10580	5895
0.5	0.971	0.971	8128	8128
0.6	0.981	0.967	6021	10810
0.7	0.975	0.917	4058	13683
0.8	0.968	0.792	2334	16854
0.9	0.971	0.524	930	20284

Table IVb. Thermodynamic properties of the Ga₂S₃ - S system calculated at 1473 K.

x_{S}	a_{S}	$a_{\text{Ga}_2\text{S}_3}$	G^{ex}_{S}	$G^{\text{ex}}_{\text{Ga}_2\text{S}_3}$
0.3	0.839	0.949	12595	3727
0.4	0.949	0.971	10580	5895
0.5	0.989	0.989	8353	8353
0.7	0.989	0.966	4233	14321
0.8	0.972	0.918	2385	17250
0.9	0.971	0.524	930	20284

A further problem connected with this approach (45, 46) is the fact that the liquidus line is usually not fully determined in the whole region and thus care must be directed to its correctness when using any of the results.

For the sake of simplicity, however, we can approximate its high temperature part as shown in Fig. 1. The results of the predicting method for both Sb-S subsystems at the fixed temperatures of 1073 and 1223 K are given in Tables IIIa and IIIb respectively. A very strong positive deviation from the Raoult law is evident and is responsible for the separation of the components.

The results obtained when a similar approach was applied to the Ga-GaS and GaS-S subsystems are listed in Tables IVa and IVb.

DISCUSSION AND CONCLUSION

Increasing attention has been paid to the thermodynamics of the III-V type semiconductor crystals (37-40, 50-53) particularly through a description of the data (13,17,18,36,37,41,48-54) for promising GaSb system (1,18). In our previous study (17) we applied the method of Gibbs energy minimization to find the critical sulphur solubility (17,18), analysed the Ga-Sb-S system with the use of what are as yet unconventional equilibrium potential diagrams (18) and estimated thermodynamic and thermochemical data using a computer simulation program (48). Our cluster theory showed (59) that a_{Ga} behaves as an ideal solution while a_{Sb} has a considerable deviation from ideality similar to that listed in Table I. It confirmed that the sulphur activity data, already published for both the Ga- and Sb- solutions, show rather scattered values over a wide range of γ (cfr. Table I). This points also to the ambiguousness of various treatments.

A very strong positive deviation from the Raoult law follows from Tables I, II and III, which clearly designate the separation of components into two layers in agreement with the phase diagrams employed, see Fig. 1. Because of the fact that we are not sure about a precise location of liquidus lines, all these results must be accepted with a certain degree of caution.

On the one hand we can compare the compiled data listed in Table I for the temperature of 985 K using the resulting value of the averaged limiting activity coefficient which reads $\ln \gamma_{\text{mean}} = -14.25$ for Ga-S and $= -5.71$ for Sb-S. However, the average data derived on the basis of our calculations are $\ln \gamma_{\text{mean}} = 0.6$ for Ga-S at 1473 K and $= 0.9$ for Sb-S at 1073 K the positive values being due to the above-mentioned positive deviation from the Raoult law. Such a considerable disagreement is partly due to temperature differences as great as 500 K, the fact that only a part of the system not covering a whole phase diagram is considered and last but not least the methods of calculation.

On the other hand we can compare our data for the $x_{\text{Ga}} = x_{\text{Sb}} = 0.5$ at $T = 1000$ K (Table II) where $\Delta G^{\text{ex}} = -2240.5 \text{ J mol}^{-1}$, with the literature data of $7095.5 \text{ J mol}^{-1}$ (27) obtained by the Li and Chou equation:

$$\Delta G^{\text{ex}} = -x_{\text{Ga}} x_{\text{Sb}} (4392 + 17022 x_{\text{Sb}} - 165138 x_{\text{Sb}}^2) \text{ J mol}^{-1} \quad (8)$$

This result is evidently in a considerable disagreement while the corresponding value of -715.8 , calculated with the use of the Readdy and Heitra equation (41):

$$\Delta G^{\text{ex}} = x(1-x)((1-x)(a_1 + a_2 T + a_3 T \ln T) + x(a_4 + a_5 T + a_6 T \ln T) + x(1-x)(a_7 + a_8 T + a_9 T)) \quad (9)$$

agrees (transferring a_i as the numerical constants from (41)). This certainly indicates some artifact in the equation (8).

In conclusion, component activity calculations based on phase diagrams is an acceptable way of obtaining values, particularly in situations where the activities required are absent and the relevant experiments difficult. There are at least two methods that may be used to calculate activities from a phase diagram involving intermediate compounds. They require, however, a different extent of additional thermodynamic information, such as the Gibbs energy or enthalpy of formation, partial molar enthalpy etc. The method used above requires only a value for the entropy of formation of the intermediate compound, which can easily be obtained in most situations. Therefore this method can play a useful role although the resulting data are apparently not in a satisfactory agreement with the literature. The source of data scatter between the different sources, treatments and interpretation schools are the subject of our further communication.

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