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COPPER SOLUBILITY AND DISTRIBUTION IN DOPED GaSb SINGLE CRYSTALS

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Abstract

For the GaSb single crystals doped with copper (grown using the Czochralski method without encapsulant in flowing atmosphere of hydrogen) the distribution coefficient of copper in GaSb, k_{eff} = 0.0021±0.0006 was found and the copper solubility in GaSb was discussed. The region of copper solubility in GaSb was analyzed on the thermodynamic basis using chemical phase diagram in the Sb–Ga–Cu system. Due to a rather low solubility of copper, its excessive amount in GaSb caused probably an increase of the dislocation density at the end of the GaSb single crystals.

Keywords: GaSb single crystals, phase diagram, Sb–Ga–Cu system

Introduction

Gallium antimonide (GaSb) is counted among very important compounds of III–V semiconductors. Unfortunately, undoped GaSb always exhibits a high concentration of residual acceptors (about 1.7×10^{17} cm^{-3} [1]) which were identified as the vacancy (V) complexes $V_{Ga}Ga_{Sb}$ [2] with very low resistivity (about $10^{-2}\Omega\cdot$cm). For the application reasons, the preparation of GaSb wafers with the low concentration of carrier concentration ($<10^{14}$ cm^{-3}) and with the high resistivity (about 10^7 $\Omega\cdot$cm) is a very important technological step. It has been supposed that the creation of semiinsulating (SI) materials is possible when metallic precipitates are presented in the semiconductor in a sufficient concentration causing the overlap of space charge regions that are formed when a metal and a semiconductor are in contact [3]. It has been found that GaP and InP become SI after copper diffusion treatment [4–7]. On the basis of this proposal

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we have tried to adopt our preparation technologies to be applicable to other III–V compounds such as GaSb.

Because of the GaSb low melting point (984 K), it was possible to carry out the Cu-diffusion at a maximum temperature of 970 K. However, after few days treatment, the thickness of layer was less than 0.5 mm and the Cu-diffusivity in GaSb at this temperature was found insufficient to produce satisfactorily thick layers of GaSb:Cu. For this reason we attempted to prepare GaSb single crystals directly doped with copper.

Experimental

GaSb as grown using the Czochralski method without encapsulant in a flowing atmosphere of hydrogen which suppresses the creation of an oxide scum on the melt surface [8, 9]. From elements (6N Ga and 6N Sb) pre-synthesized GaSb was used as a starting material. Before the crystal growth, GaSb polycrystalline bowl was cleaned by grinding and etching in an acid solution. Copper was added in an elementary form in an amount of 9.56×10^{18}–9.56×10^{19} atoms $\cdot$cm^{-3} in the starting melt. The <111> GaSb single crystals were grown using the method and growth conditions described in detail in our previous paper [9].

In order to study the influence of copper on the resistivity of GaSb, the crystals were cut to samples with a thickness of about 1 mm. The Hall concentration was measured using the van der Pauw method to within ±5% accuracy in the magnetic field up to 0.4 T. The temperature dependence of Hall effect was carried out in the range of 77–300 K. As a supplement to the electrical measurement the dislocation density (EPD) was calculated on the wafers which were first mechanically polished and then chemically etched. The method of this treatment was described elsewhere [9].

Distribution of copper in GaSb

Copper behaves as a p-type dopant. Unfortunately the resistivity of GaSb has not increased (Table 1) as we supposed on the basis of similarity with the other III–V compounds doped with copper [4–6].

For this reason we have paid an increased attention to the evaluation of the distribution coefficient of copper (k_{eff}) in GaSb which was not published yet, and, on the other hand, to the estimation of the solubility region of copper in GaSb.

For the calculation of k_{eff} we applied the Pfann equation [10] which is very useful and describing the distribution of impurities in GaSb very well as it was already found out for other dopants [11, 12]. In the first step we calculated the Cu-concentration from the free carrier concentration. We assumed that all the

Table 1 Some properties of the GaSb single crystals doped with copper

Starting concentr. in the melt/ atoms $\cdot cm^{-3}$	Solidifying fraction x	Hall concentr./ cm^{-3}	Concentr. of copper/ atoms ·cm–3	Mobility/ $cm^2 \cdot V^{-1} \cdot s^{-1}$	Resistivity/ $\Omega \cdot cm$	Distribution coefficient k_{eff}
9.56×10^{18}	0.30	1.99×10^{17}	0.29×1017	515	0.058	0.0022
	0.65	2.47×10^{17}	0.77×1017	536	0.043	0.0029
9.56×10^{19}	0.30	3.76×10^{17}	2.06×1017	582	0.039	0.0016
	0.65	4.81×10^{17}	3.11×10^{17}	525	0.031	0.0015

Cu-atoms soluted in GaSb crystals are ionized at the lower Cu-concentrations. Therefore an increase in the free carrier concentration in Cu-doped against undoped GaSb is caused by Cu-dopant, i.e. the concentration is expressed by thedifference between the free carrier concentration in Cu:GaSb and in undoped GaSb which is 1.7×10^{17} atoms·cm^{-3} [1].

Using the calculated concentrations of copper, the distribution coefficient was evaluated by means of the normal freeze equation [10] which was treated by an iteration method for each measured solidifying fraction (x) and the corresponding Cu-concentration in the solid GaSb and the Cu-concentration in the starting melt.

The distribution coefficient of copper in GaSb is 0.0021±0.0006 with an accuracy of 28%. The spreading of copper in GaSb along the growth direction was in good agreement with the theoretical profile calculated from the Pfann equation. It is necessary to add that the distribution of copper over the sample surface was homogeneous in the whole range of the used starting concentration of copper. No facets were observed. We suppose that the creation of the inhomogeneity of dopants in the perpendicular direction to the growth direction is caused by its relatively high concentration in GaSb [8]. In the case of the very low distribution coefficient [12] the values of the dopant concentration are low almost in the whole crystal bowl ($x<0.9$) and therefore any concentration discrepancies did not appeared.

The dislocation density (EPD) was measured by the chemical etching along the growth direction (i.e. in the <111> direction). Close to the seed, EPD was very high ($>10^3$ cm^{-2}) as it is conventionally in the case of the crystals grown in the <111> direction [13, 14]. After 5 millimeters EPD rapidly decreased to a value of $<10^2$ cm^{-2} and then it did not change in the length of about 20 mm. The homogeneity of dislocations on the surface of the samples was very good in the first part of the crystals, but in the second half of the crystals (the crystals have a length of about 60 mm), the distribution of EPD has changed markedly because islands with a high EPD (about 10^4 cm^{-2}) started to appear suddenly and enlarged with the growth length of the crystals. The places among these islands were dislocation-free but became smaller. At the end of the crystals, the dislocation density reached a value of about 10^5 cm^{-2} and the distribution of dislocations was almost uniform.

Such island destroyed structures were cut out from the wafers and their carrier concentration was measured. However, its value was the same as in the part without dislocations and the higher concentration of copper was neither identified by the electrical measurement.

Presentation of thermodynamic properties and construction of chemical potential diagrams in the Ga–Sb–Cu system

The second aim of our study of GaSb crystals doped with copper was to find out the existence region of copper-based phases in the vicinity of GaSb compound. For this purpose we first investigated a standard view of phase diagrams in Sb–Ga–Cu pseudobinary alloys Ga–Cu [15, 16] and Sb–Cu [17, 18].

It can be found [19] that on the Sb side there is no Cu solubility [15, 16] and on the Ga side, the low temperature melting hides any possible traces of Cu solubility [17, 18]. There are no data on GaSb but we may anticipate that the Cu solubility is also negligible.

When the standard enthalpy for formation, d_fH°, the standard entropy, S°, at 298 K, and high temperature capacity, $C_p(T)$, are all available, the Gibbs energy for formation at any temperature can be calculated as follows:

$$d_fG^\circ = d_fH^\circ + T(S^\circ + \left(\int C_p/T\,dT + (1/T)\int C_p\,dT\right)$$

Table 2 lists the thermodynamic properties used in the present investigation on the Ga–Sb–Cu system; they were taken from the thermodynamic database MALT2 which is based mainly on the NBS tables. We, however, did not take into account the β-phase of Cu_3Sb exhibiting the Sb solubility region between about 19 to 31% Sb and existing from 718 K to its peritectic melting point of about 956 K. On the Ga-side [19], there are known both the γ-phase of an approximate stoichiometry of Ga_4Cu_9 melting peritectically at 1109 K and also the region of a substantial solubility of Ga in Cu up to about 20.5 at.% Ga.

The chemical potential diagrams [26, 27] for the Ga–Sb–Cu system, see Fig. 1, were constructed using the computer program which can provide any selection of the axis variables. In the present study, a $\log(a(\mathrm{Ga})/a(\mathrm{Cu}))$ *vs.* $\log P(\mathrm{Sb_2})$ plot was adopted because the Sb partial pressure is one of the major controlling factors in experiments and also because the logarithmic activity ratio of Ga to Cu is appropriate to treat both elements in an equivalent way. In this plot, the stability polygon of GaSb has a certain range of the Sb potential and can also be represented by the activity ratios $a_{\mathrm{Cu}}/a_{\mathrm{Ga}}$ *vs.* $a_{\mathrm{Sb}}/a_{\mathrm{Ga}}$. This corresponds to different states of the doped copper GaSb. Although these diagrams are constructed by using only the thermodynamic data of compounds, the stability polygon of the respective compounds yields information on impurities or dopants within the infinitely dilute solution approximation. This means that each point of the polygon of GaSb indicate implicitly its respective dopant level of copper.

When the thermodynamic effects of doping are explicitly considered, the polygon of GaSb is slightly modified so that the three phase (GaSb–Cu_2Sb–Sb)

Table 2 Thermodynamic data for Sb, Ga, GaSb, Cu and Cu_2Sb

Substance	State	d_fH/	d_fG/	S/	C_p equation					T_{tr}/	$d_{tr}H$	References
		$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	a	b	c	d	e	K	$kJ \cdot mol^{-1}$	
Sb	c	0	0	45.69	30.54	−15.56	−2.01	18.07		904 *mp*	19.87	[21, 22]
	l				31.38							[22]
Ga	c	0	0	40.88	26.15					303*mp*	5.59	[21, 23]
	l				25.26	0.68	3.98	0	−0.43	2474*mp*	258.76	[23]
GaSb	c	−41.80	−38.90	76.07	45.52	11.465	−0.359			985*bp*	65.10	[21, 24]
	l				62.76							[24]
Cu	c	0	0	33.15	26.74	−2.59	−1.76	4.87		1356*mp*	13.14	[21, 25]
	l				32.84							[25]
Cu_2S	c	−11.70	−16.02	126.48	68.29	27.61				374*tp*	2.22	[19]
	l				68.29	27.61				859*pp*		

c-solid, l-liquid, T_{tr}-transformation temperature at *mp*-melting point, *bp*-boiling point, *tp*-transformation point, *pp*-peritectic point.

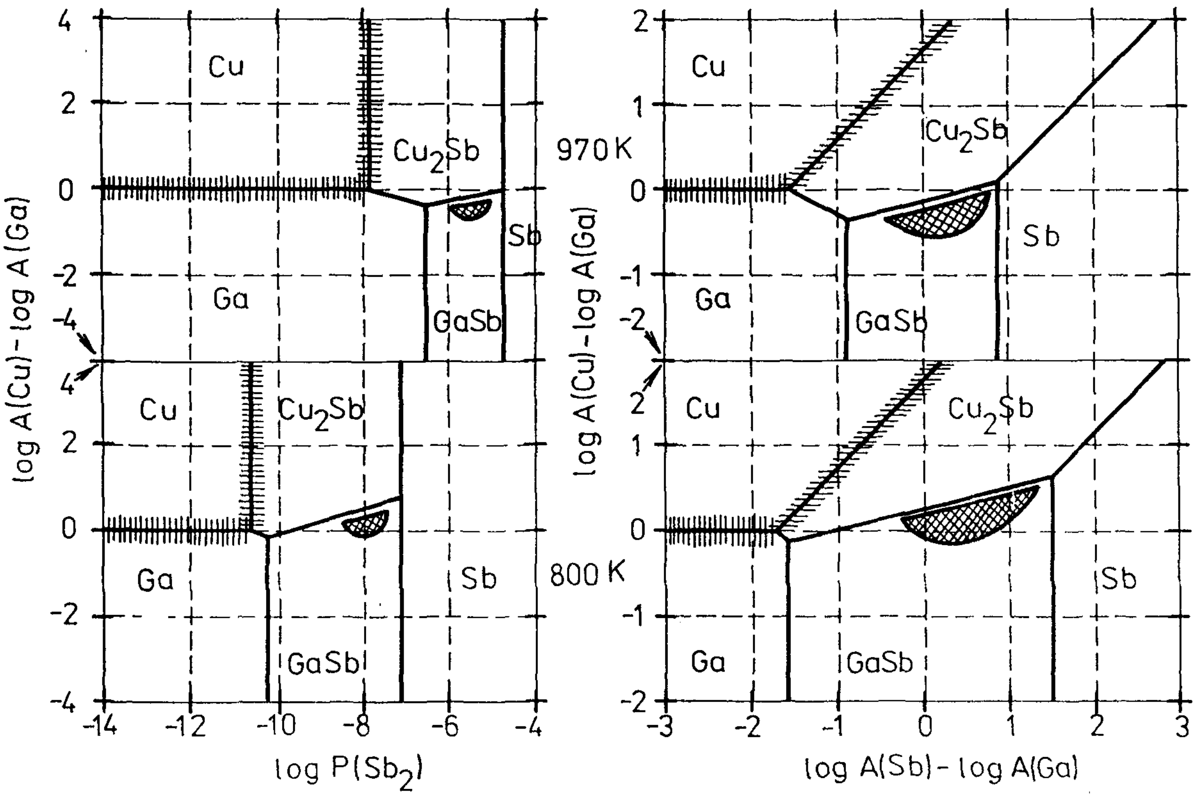

Fig. 1 Chemical potential diagrams for the Sb–Ga–Cu system at 970 and 800 K where the stability areas of the Cu, Ga, GaSb, Cu_2Sb and Sb are bounded while the possible existence of the intermetallic Cu:$Ga_{(ss)}$, Cu_3Sb and Cu-doped GaSb are marked by vertical, horizontal and intercrossed lines, respectively

junction moves to the high Sb potential region. Since the effect of extension of the stability polygon by the explicit treatment of solid solution is in the order of 0.1, it is expected that the solubility limit of copper is very small and highly Cu doped GaSb will decompose, forming Cu_2Sb and Sb.

Conclusion

We have experimental approved our thermodynamic calculations concerning a very limited solubility of copper in GaSb single crystals. Our measurements, however, did not provide any clear basis to estimate reasons for a sudden enlargement of EPD in the GaSb crystals doped with copper. We can suppose that the dislocation rich islands were created by means of the increased concentration of copper being segregated in the second (possibly Cu_2Sb) phase probably because the solubility of copper in GaSb was exceeded. Copper in this form may behave as an electrically inactive phase. This assumption is certainly a simplification and is evidently unsatisfactory to fully explain the origin of the effect which has occurred in the GaSb crystals doped with copper and which is under our further studies.

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Zusammenfassung — Für mit Kupfer versetzte GaSb-Einkristalle (gezüchtet nach der Czochralski Methode ohne Einbettung in dynamischer Wasserstoffatmosphäre) wurde der Verteilungskoeffizient *für Kupfer in GaSb mit* k_{eff} *= 0.00210.0006* ermittelt und die Löslichkeit von Kupfer in GaSb diskutiert. Mittels chemischen Phasendiagrammen des Systemes Sb–Ga–Cu wurde auf thermodynamischer Grundlage der Bereich der Kupferlöslichkeit im GaSb System analysiert. Wegen der eher geringen Löslichkeit von Kupfer verursacht seine Überschußmenge in GaSb ein Ansteigen der Versetzungsdichte am Ende von GaSb-Einkristallen.