Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 749-754

DOPING LIMITS AND GROWTH THERMODYNAMICS OF GaSb CRYSTALS

J. Šesták, V. Šestáková and B. Štěpánek

Division of Solid-State Physics, Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Prague - 6, Czech Republic

Abstract

Beside four approaches to the thermodynamics of GaSb–M(=S,Te) solid solutions the doping limits for extremely narrow concentration regions are analysed and ranked in the Cu, Ge, Mn (p-dopants), S, Se, Te (n-dopants) and N, In (isoelectric) groups.

Keywords: Cu, doping, GaSb, Ge, Mn, S, Se, semiconductors, solubility, Te, thermodynamics

Introduction

The technology of the crystal growth made a wide progress during 20 last years which has essentially decreased prices of semiconductor production, improved quality of semiconductor devices and enabled their dissemination in all our live. For an example, the silicon crystals grown from the melt in diameter of 2.5 cm 20 years ago are presently prepared in 15–20 cm diameter with a dislocation density almost close to zero.

The most helpful scientific field, which has shared many successes of the growth technology is and will be the thermodynamics. Many examples can be shown where the thermodynamics played a significant role in the preparation of perfect silicon crystals, silicon wafers and assisted to solve the crystal doping. It is worth noting, however, that the semiconductor industry also fabricates another materials which are equally important in the construction of different electronic and optoelectronic devices. The advanced semiconductor compound is GaAs and the thermodynamics solved in this field the series of technological problems such as a decrease of impurities concentration, prevention of its oxidation as well as reduction of GaAs dislocation density.

The optimal solution of technological shortcomings were not found until the thermodynamic analysis was applied. After providing successful thermodynamic calculations, the thermodynamic methods came successfully into the technology of single crystal growth because it threw new light on the behaviour of low concentration in the multicomponent compounds and thus helped their preparation. The thermodynamics shown its very important role in solving various technological problems and becomes attractive for technologists in preparing a wide spectrum of semiconductor materials in wide III–V, IV–VI and II–VI compound families.

1418–2874/99/ $ 5.00

© 1999 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest

Kluwer Academic Publishers, Dordrecht

Thermodynamics and GaSb growth

Thermodynamic methods and evaluations have been applied at our Institute of Physics in Prague and helped to find the solutions in preparation of new kinds of semiconductor single crystals needed for future physical measurements and applications. The one of most important problems was to define a method how to predict behaviours of dopants in very low concentrations, i.e., in the range of $1\cdot10^{16}$–$1\cdot10^{19}$ atoms cm^{-3} which is effectively 0.01–0.00001% dopant in the starting material. Several years ago, we faced the request of physicists who wanted to measure GaSb single crystals doped by sulphur while seeking new material for lasers and detectors in the IR range up to 2.3 μm wavelength. The thermodynamic calculations enabled us to describe and to find the optimal method of the growth of GaSb crystals with sulphur concentration of $1\cdot10^{16}$–$1\cdot10^{17}$ atoms cm^{-3}. In addition, the used thermodynamic methods helped us to explain the double doping of tellurium and sulphur and for this reason our technology was able to prepare these GaSb crystals with various concentrations of both elements.

The research on GaSb single crystals has continued and in the present time it seems to be important and useful because this material will likely serve as a further semiconductor material for a fabrication of new electronic and optoelectronic devices applicable in a wider range of utilisation. For this reason we have tried to bring the thermodynamic calculations in our technological methods and with their help to find save, optimal and successful solutions for preparations of perfect GaSb single crystals with predicable and reproducible behaviours.

GaSb has a melting point of 712°C, which is substantially lower than that of GaAs at 1240°C. The loss of Sb at moderate temperatures and the easy formation of surface scum [1] by gallium oxides are often cited as a most difficult processing problem. In contrast to Al–Ga–Sb compounds with high Al contents the material is stable against oxidation by water vapour. The growth of S-doped GaSb was reported earlier [2–4]. 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, 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 volatilisation and help to preserve the stoichiometry of the grown crystals. For a standard preparation of the GaSb single crystals [2, 5–8] (grown by the Czochralski method without encapsulant in a hydrogen atmosphere) the S-concentration (calculated from Hall measurements) reached a limited value of $1\cdot10^{17}$ atoms cm^{-3} in the crystals despite the fact that the starting amount in the melt exceeded about $2\cdot10^{20}$ atoms cm^{-3}. It seems that the evaporation begins at the 7.2 ppm level already mentioned (0.0043 at.%) [9]. The S-concentrations, however, were from 0.0035 to 1.112 at.% [2] 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.

Thermodynamics of GaSb

The survey of basic thermodynamic data was already published in [10–12]. Some actual calculations were provided for standard binary and ternary mixtures using:

a) Yokokawa's constructions of isothermal diagrams of phase stability (i.e. chemical potential diagrams) [10, 14],

b) qualitative approach based on Voňka and Leitner's calculations of coexistivity phases [10,13],

c) estimation of activity data using Zivkovic and Chou's treatment [15],

d) Moiseev and Šesták's simulation methods estimating standard thermodynamic data [11, 12].

Such scientific treatments, however, did not provide adequate data for an extremely narrow concentration region within which the actual doping of GaSb is usually realised {method (b) for sulphur [13]}.

The most widely studied Ga–Sb–S solid solution was, for example, presumed to be a pseudobinary solution of the components GaSb and S. The value of the limiting activity coefficient of sulphur in this solution was estimated by the Kroger equation [13]. For determining the sensitivity of the calculated results on the used thermodynamic data the equilibrium calculations were carried out using both the highest and lowest values of the limiting activity coefficient of sulphur {for the GaSb equilibrium distribution coefficient, $k^{\circ}_{S(GaSb)}$=0.1 and 0.01}. From the compensation and the indefiniteness of initial thermodynamic data it followed that the calculated results concurred but were of rough estimate, only. The thermodynamical calculation were, however, in a good agreement with our previous experiments when growing the S-doped GaSb single crystals and the maximum attainable concentration of sulphur in the single crystals bowl was agreeable about 10^{17} atoms cm^{-3}. Practically when this value is exceeding the grown crystals became either polycrystalline or twinned.

Actual GaSb doping

The actual doping data and doping limits of various elements are summarised in the Table 1. It is necessary to add some other data on mobilities and free carrier concentrations available from our growth experiments [16, 17]. The GaSb crystals were grown under different doping procedures during the Czochralski method and the introduced dopants can be roughly ranked into the three categories:

a) typical p-dopants, such as Cu, Ge, Mn [16, 19] and the other elements used in diffusion method. They cause an increase of p-concentration and decrease the mobility, e.g., the GaSb:Mn crystals showed p=(4–50)$\cdot 10^{17}$ cm^{-3} and μ=(400–600) $cm^2/(Vs)$ [20],

b) typical n-dopants, such as S, Se, Te and co-doping Te+S. They compensate natural defects and cause an increase of n-concentration and substantially increase the mobility, e.g. the GaSb:S crystals showed p={1–(–3)$\cdot 10^{17}$ cm^{-3} and μ=(600–2500) $cm^2/(Vs)$ [2], while for the GaSb:Se these values were found n=(1–50)$\cdot 10^{17}$ cm^{-3} and μ=(2000–

2500) $cm^2/(Vs)$ [20]. The GaSb:Te showed the values n=(1–100)·10^{17} cm^{-3} and μ=(2500–3500) $cm^2/(Vs)$ [2] and the similar results have been obtained in the case of co-doping of Te+S [6],

c) isoelectric dopants, such as N and In do not influence the electrical behaviours and are only effective on the structure perfection of as-grown crystals. For this reason the p-concentrations and mobilities for N and In are almost the same as in the case of the undoped crystals (p≈1.5·10^{17} cm^{-3} and μ=(600–650) $cm^2/(Vs)$ [20].

Table 1 Distribution coefficient and doping limits of the dopants in the GaSb single crystals grown by the Czochralski method

Dopant	Concentration limit	Distribution coefficient (k_{eff})
Cu	$3\cdot10^{17}$	0.0021
Zn	$2\cdot10^{19}$	0.30
Cd	$5\cdot10^{18}$	0.02
In	$>5\cdot10^{20}$	1
Si	$3\cdot10^{19}$	~1
Ge	$5\cdot10^{20}$	0.32
Sn	$5\cdot10^{17}$	0.010
N	$\sim1\cdot10^{17}$	0.4–0.8
As	$\sim1\cdot10^{21}$	2–4
S	$4\cdot10^{17}$	0.06
Se	$5\cdot10^{19}$	0.35
Te	$\sim5\cdot10^{20}$	0.32
Mn	$5\cdot10^{18}$	0.011

It is worth mentioning that the measurement of the structure perfection, namely dislocation density, is a very important point of the study and understanding of the doping procedure. The dopants influence not only electrical and optical behaviours but also the structure, effect concentration of defects and determine the quality of as-grown GaSb crystals. This problem was discussed elsewhere [2, 6, 13, 16, 19–24]. The dopants were described to substantially improve the crystallographic structure, such as Te [24], or impair the single crystalline growth, such as Cu and N [16, 21] or cause the rapid growth of a dislocation density. To improve the passivation of impurities (natural impurities and defects and added dopants) [25] the growth of doped GaSb crystals was run under an ionized hydrogen atmosphere. The deuterium lamp was situated in such a position that the stream was focused about 1 cm above the solid/liquid interface which was seemed to be most effective.

Conclusions

The doping limits and effective distribution coefficients of the measured dopants (elements) are summarised in the Table 1. The Czochralski methods without encapsulant in a flowing hydrogen atmosphere did not enable to change a pressure of ambient atmosphere in a wider range (only within $(1.0-1.3)\cdot 10^5$ Pa). For this reason it was necessary to assume that the doping limits of the volatile elements such as N, As, S, Se and also Te, appeared rather greater than we estimated. The higher pressure of ambient mixture of inert gas and doping element in the growth system should prevent an evaporation of doping elements from the melt, and thus increase, its solubility in the solid state. In addition, with achieving a low dislocation density and the absence of parasite crystals the level of doping should be as high as possible. The structure of such grown crystals would become more perfect, because the growth procedure on the surface contact between the liquid and solid would not impair with evaporation effects.

Our results correspond with other authors working on the same system. However, it is worth noting that only few data of solubility limits were shown in the literature and for this reason we suppose that it would be helpful and more precise to measure the concentration limits by means other complementary methods like DLTS, chemical analysis, etc.

The next step of our thermodynamic treatment [26] will be the analysis of our preliminary calculated S–Ga–Sb–H system in which the ionized hydrogen (H^+) will be added. It is hoped to help solving problem of the compensation of natural defects (acceptors) having *p* type conductivity and/or donors coming either from residual impurities or intentionally doped. According to our measurements and our assumption, the donors are preferably passivated and it seems that the equilibrium between the passivated and active donors into the GaSb structure is creating. That should be solved by the thermodynamics methods.

* * *

The study was carried out under the sponsorship of the Grant Agency of the Czech Republic Nr. 104/97/0589 and Nr. 100/98/0024.

References

1 B. Štěpánek, V. Šestáková and J. Šesták, Inorganic Materials, 29 (1993) 1071.
2 B. Štěpánek, V. Šestáková, P. Hubík and V. Charvát, J. Crystal Growth, 126 (1993) 617.
3 B. Štěpánek, V. Šestáková and J. Krištofik, Cryst. Res. Technol., 29 (1994) 19.
4 K. B. McAfee, D. M. Gay, R. S. Hozack, R. A. Laudise, G. Schwartz and W. A. Sunder, J. Crystal Growth, 76 (1986) 263.
5 M. Lee, D. J. Nicholas, K. E. Singer and B. Hamilton, J. Appl. Phys., 59 (1986) 2895.
6 P. Hubík, V. Šmíd, J. Krištofik, B. Štěpánek and V. Šestáková, Solid State Commun., 86 (1993) 19.
7 V. Šestáková and B. Štěpánek, Thermochim. Acta, 198 (1992) 213.
8 B. Štěpánek and V. Šestáková, Thermochim. Acta, 209 (1992) 285.
9 V. Šestáková, B. Štěpánek, P. Hubík and V. Šmíd, Mater. Sci. Eng., B21 (1993) 14.
10 J. Šesták, J. Leitner, H. Yokokawa and B. Štěpánek, Thermochim. Acta, 245 (1994) 189.

11 G. K. Moiseev and J. Šesták, J. Thermal Anal., 43 (1995) 539.
12 G. K. Moiseev and J. Šesták, Prog. Cryst. Growth and Character., 30 (1995) 23.
13 B. Štěpánek, V. Šestáková, J. Šesták and J. Leitner, Semiconduc. Sci. Technol., 9 (1994) 341.
14 J. Šesták, B. Štěpánek, H. Yokokawa and V. Šestáková, J. Thermal Anal., 43 (1995) 389.
15 J. Šesták, V. Šestáková, Z. Zivkovic and D. Zivkovic, Pure & Appl. Chem., 67 (1995) 1885.
16 V. Šestáková and B. Štěpánek, Mater. Sci. and Eng., B28 (1994) 138.
17 J. Mimkes, V. Šestáková, K. M. Nassr, M. Lübbers and B. Štěpánek, J. Crystal Growth, 187 (1998) 355.
18 K. M. Nassr, M. Lübbers, V. Šestáková and J. Mimkes, J. Therm. Anal. Cal., 54 (1998) 355.
19 V. Šestáková and B. Štěpánek, J. Crystal Growth, 146 (1995) 87.
20 V. Šestáková, P. Hubík, B. Štěpánek and J. Krištofik, J. Crystal Growth, 132 (1993) 345.
21 B. Štěpánek and V. Šestáková, J. Crystal Growth, 123 (1992) 306.
22 F. Moravec, V. Šestáková, B. Štěpánek and V. Charvát, Crystal Res. Technol., 24 (1989) 275.
23 V. Šestáková, B. Štěpánek and J. Šesták, J. Crystal Growth, 165 (1996) 159.
24 V. Šestáková, B. Štěpánek and J. Šesták, Czech. J. Phys., in print.
25 V. Šestáková, B. Štěpánek, J. J. Mareš and J. Šesták, Mater. Chem. Phys., 45 (1996) 39.
26 J. Leitner and J. Šesták, 'Thermochemical and Thermodynamic Properties of Solids: Theoretical Thermodynamics, Thermal Analysis and Calorimetry', book in the course of Preparation, Academia Prague, 1999.