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Czochralski grown concentration profiles in the undoped and Te-doped GaSb single crystals

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Abstract

A series of undoped and Te-doped GaSb single crystals were grown by means of the Czochralski technique without encapsulant in a flowing hydrogen atmosphere. It was found that the concentration of residual acceptors is $\approx 1.7 \times 10^{17}$ atoms cm^{-3} not including the concentration of the original impurities. It was shown that the increment of Te concentration along the growth direction is very well described by the normal freeze equation (Pfann equation), but the limiting concentration of tellurium in the starting melt is about 8.0×10^{17} atoms cm^{-3}. In the case of higher Te concentrations, the measured free carrier concentration is always lower than that calculated from the Pfann equation.

INTRODUCTION

The gallium antimonide single crystal is one of the III–V compounds used as a substrate material. It is used for the fabrication of long wavelength detectors and lasers. High quality GaSb substrates are required for the growth of (GaIn)(AsP) layers used in the field of optical communications. The use of these longer wavelengths ($\lambda \gtrsim 1.5$ μm) makes it possible significantly to reduce losses due to Rayleigh scattering. GaSb is an interesting material and it has a very small difference of lattice parameters in comparison with other ternary or quaternary substrates comprising III–V compounds which are suitable for this wavelength region [1].

For epitaxial growth it is necessary to have GaSb substrates with definite types of impurities, specific concentrations and free carrier concentration. GaSb single crystals are therefore doped with different elements (e.g. Te, Se, Ge or Zn) [2].

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During the growth of single crystals from the melt the concentration of impurities (dopants) is changing [3]. If the distribution coefficient of a dopant (k_{ef}) is lower than 1 ($k_{ef} < 1$) the impurity concentration increases from the beginning to the end of the crystal, and vice versa. The carrier concentration changes in the same direction.

However, the concentration of residual acceptors in an undoped GaSb single crystal according to the literature [3–11] is $(1.0\text{–}2.7) \times 10^{17}$ atoms cm^{-3}, either because of residual impurities or antisite defects, or due to crystalline nonstoichiometry. These crystals show p-type conductivity. By using a donor impurity (e.g. Te) it is possible to change p-conductivity to n-type in the growing process.

The carrier concentration can very easily be measured by the van der Pauw method [12], and the impurity concentration can be determined, for example, by means of atomic absorption analysis [10]. However, for the growth of single crystals with a definite carrier concentration and a given type of conductivity, we have to know the exact correlation between the concentration of impurities (which we deliberately put into the starting material or melt) and the consequent carrier concentration. In addition, it is necessary to know the distance from the beginning of the grown crystal where the cut wafers would show the required carrier concentration. Consequently, we have to find how the distribution of carrier concentration is dependent on the pulling direction of the single crystals. For this reason we can economize on GaSb material, and it is not necessary to look for a suitable wafer and carry out a lot of superfluous analysis before an acceptable substrate will be found.

A relationship between the concentration of impurities in a melt and in a crystal exists [3, 13] but the practical correlation in rigorous and opinions as to the relationship differ [10, 13–15].

The aim of our investigation is the development and study of the correlation between the theoretical relationship and the practically measured carrier concentration in the case of Te-doped GaSb single crystals grown by the Czochralski method.

CRYSTAL GROWTH

The Czochralski technique without encapsulant is a very suitable method for the growth of compounds with a low vapour pressure of the volatile components, GaSb being one such material. The vapour pressure of antimony is about 100 Pa at the melting point of GaSb (712°C). About 1×10^{-3} mol of antimony would be lost because of the inert gas passing through the puller with a flow rate of 70 $\text{cm}^3\,\text{min}^{-1}$ for a run of about 10 hours. Because the melt used contains about 1 mol of antimony it is necessary to compensate for the volatilization of antimony by adding about 0.1% to the starting material [16].

For our study two kinds of starting material were used: (a) polycrystalline material from Spurmetalle Freiberg (Germany) (Freiberg GaSb material); (b) material made by us by means of direct synthesis from the elements (6N Ga and 5N5 Sb) in an LEC apparatus (with B_2O_3 encapsulant) at 8 MPa pressure of argon and at a temperature of about 900°C (synthetic GaSb material).

The Czochralski apparatus used was described in the previous paper [16] (Fig. 1). Both kinds of starting material were cleaned by grinding and etching in a solution of acids (6 parts HNO_3 + 2 parts HF + 1 part CH_3COOH), followed by distilled water rinses, and were put into a quartz crucible. For doping, elementary tellurium (6N Te) was added to this charge (170 g) in an amount of 0.0006–0.03 g.

From a very good quality undoped GaSb single crystal the seed was cut at a length of about 5 cm having the dimensions 4 mm × 4 mm with an orientation of ⟨111⟩*b*(Sb) to the melt.

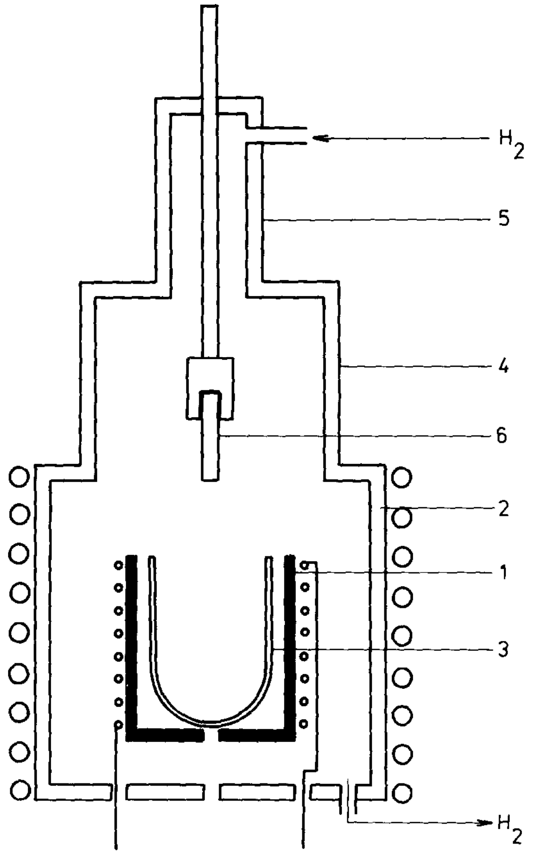

Fig. 1. Schematic diagram of the Czochralski apparatus for GaSb growth. 1, graphtite cylinder with molybdenum wire coils; 2, water cooled brass cylinder; 3, quartz crucible; 4, quartz tube; 5, top part of apparatus; 6, seed.

The whole growth process (melting, growing and cooling) was carried out in a flowing hydrogen atmosphere very well purified by a palladium purifier. It was found that an H_2 atmosphere is superior to inert gases because it suppresses oxide formation [10, 16, 17]. The hydrogen flow rate was kept at a value of 70 cm^3 min^{-1}. The rotation of the seed was varied in the range of 20–25 rpm and the pulling rate was 12 mm h^{-1}. The crucible with melt was stationary. Before the growth step the Czochralski apparatus was closed and purified hydrogen was passed through during 24 h at room temperature to purify the whole system.

Using the same growth conditions, undoped GaSb single crystals were grown from both the Freiberg and our synthetic materials. The Te-doped GaSb single crystals with different tellurium concentrations in the starting melt were pulled from the Freiberg material only.

RESULTS AND DISCUSSION

The two undoped single crystals grown from different starting materials were cut along the growth direction at a distance of 1 mm. The thickness of the wafers was 1 mm. Their carrier concentration were measured by means of the van der Pauw method to within ±3% accuracy. The dependence of carrier concentration on the growth distance (x, the solidifying fraction) from the beginning of the crystal was determined (Fig. 2, GaSb-6, Freiberg starting material). The curve was not parallel to the x-axis, but it fell slightly from $x = 0$ to $x = 0.7$. The carrier concentration then decreased rapidly. It seems that the profile of the curve follows

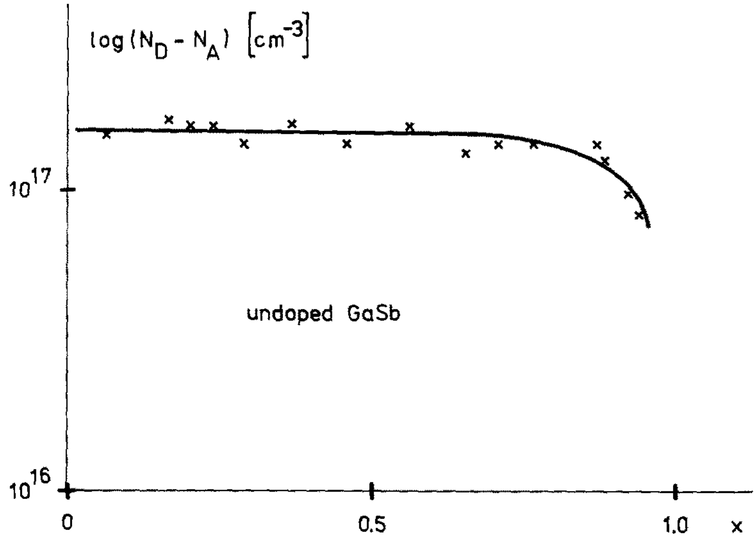

Fig. 2. Carrier concentration distributions ($\log(N_D - N_A)$) along the growth direction in the undoped GaSb single crystal: Freiberg starting material (x is the solidifying fraction).

the normal freeze equation [13]

$$C_c = C_o k_{ef}(1 - x)^{(k_{ef}-1)} \tag{1}$$

where in this case C_c is the concentration of residual impurities in the crystal, C_o is the original concentration of the impurities in the liquid (in the starting material), k_{ef} is the equilibrium distribution coefficient and x is the solidifying fraction. According to the literature [2, 18], the distribution coefficients of the elements contained in the starting material are less than 1 (see Table 1; elements with a concentration below 0.01 ppm are not listed), therefore we assume that the concentration of all impurities in our crystals increases during crystal growth in the solidified fraction. Because the concentration of the donor elements (the so-called N_D) in the starting material is higher than that of the acceptor ones (the so-called N_A) the carrier concentration decreases.

From the curves measured for two undoped single crystals we calculated the equation in the range $0 \leqslant x \leqslant 0.6$, which we can perform in this case because the carrier concentration decreases linearly (see, e.g., Fig. 2)

$$C_{(N_D-N_A)} = 1.56 \times 10^{17} - 0.078 \times 10^{17}x \tag{2}$$

for the GaSb-6 Freiberg material, and

$$C_{(N_D-N_A)} = 1.74 \times 10^{17} - 0.041 \times 10^{17}x \tag{3}$$

for the GaSb-81 synthetic material. From these equations we calculated the $(N_D - N_A)$ concentrations for $x = 0$ and $x = 0.5$. Using the measured

TABLE 1

Analysis of GaSb starting materials by means of spark source mass spectroscopy in ppm (elements with a concentration below 0.01 ppm are not listed)

Elements	Synthetic GaSb	Freiberg GaSb
N	2.078	2.359
O	7.758	12.323
Al	0.666	0.962
Si	0.213	1.282
S	0.032	0.296
Cl	0.188	0.288
K	0.049	0.101
Se	0.076	0.131
Mo	0.081	0.467
Ag	0.154	0.112
Cd	0.041	0.051
In	0.094	0.099
Sn	0.041	0.035
Te	0.069	0.011

values from Table 1 (±3% accuracy) and the normal freeze equation, we computed the theoretical values of $(N_D - N_A)$ carrier concentration for the same x, i.e. $x = 0$ and $x = 0.5$ (Table 2).

The sum of $(N_D - N_A)$ carrier concentration from eqns. (2) and (3) and from the theoretical calculation of the impurity concentration in the grown crystal is the same for each case, i.e. both for different x and for various kinds of starting material. The Freiberg material contained a higher concentration of N_D impurities than our synthesized one, and therefore the carrier concentration should have been lower. Hence it follows that the different carrier concentrations of undoped GaSb single crystals published in the literature [4–11] were the outcome of different concentrations of impurities in the starting material. Our results give an explanation for the changes of the carrier concentration in undoped GaSb along the length of the crystal in the range of 10%, as was published in [10], and also the decrement of impurity contents in the single crystal (1.1×10^{17} atom cm^{-3}) compared with that of the starting material ((2–3) $\times 10^{17}$ atom cm^{-3}) shown in ref. 6.

If the carrier concentration in undoped GaSb changes along the growth direction of the crystal, the normal freeze equation (1) [13] is valid. If the concentration of common impurities falls below 0.1 ppm in the starting material, the residual concentration will be $\approx 1.7 \times 10^{17}$ atom cm^{-3}, varying in the order of about 1×10^{15} atom cm^{-3} along the crystal growth length. Consequently, the residual value can be affected by antisite defects or crystalline nonstoichiometry [10].

We grew a second series of Te-doped GaSb single crystals with different concentrations of tellurium in the melt (9.2×10^{16} to 4.52×10^{18} atom cm^{-3}). The crystals were cut in the same way as mentioned above. The measured carrier concentrations of the wafers were again compared with the normal freeze equation. We note here, however, that the authors of ref. 10 declared that the normal freeze equation is not applicable.

TABLE 2

The theoretical contribution of the impurities in the starting material to the carrier concentration in the single crystal

$N_D - N_A$ (atom cm^{-3})	GaSb-6	Freiberg material	GaSb-81	Synthetic material
	$x = 0$	$x = 0.5$	$x = 0$	$x = 0.5$
eqn. (2) or eqn. (3)	1.56×10^{17}	1.52×10^{17}	1.74×10^{17}	1.72×10^{17}
from Table 1	1.40×10^{16}	2.01×10^{16}	1.44×10^{15}	2.40×10^{15}
Total	1.70×10^{17}	1.72×10^{17}	1.75×10^{17}	1.74×10^{17}

We substituted the Te concentration (determined from chemical analysis) for the $((N_D - N_A) - N_U)$ carrier concentration (where N_U is the contribution of tellurium) in the Pfann equation. We assumed that all the tellurium is ionized and each Te atom contributes one electron. Then we can consider C_o to be the tellurium concentration of the starting material in the eqn. (1). The carrier concentration $(N_D - N_A)$ was again measured with high accuracy (±3% at room temperature) by means of the van der Pauw method, and C_c (from eqn. (1)) is the absolute value of $|(N_D - N_A) - N_U|$. Because the Freiberg starting material was used, N_U is equal to $C_{(N_D-N_A)}$ on the basis of eqn. (2). This means that C_c is simply the contribution of tellurium (N_D). The calculated values for $x = 0.02$ are listed in Table 3.

At low concentration of tellurium in the melt, the Pfann equation (1) describes very well the course of the Te concentration as a $|(N_D - N_A) - N_U|$ carrier concentration developed along the growth direction of the GaSb single crystals; see Fig. 3. The starting concentration of tellurium in the melt was 9.2×10^{16} atom cm^{-3} and the GaSb showed p-type conductivity along the whole measured length of the crystal.

A good conformity of the normal freeze equation (1) with the N_D contribution is followed up to the starting concentration of about 8.0×10^{17} atom cm^{-3} in the GaSb melt. Above that, the difference found between the measured values and the calculated concentrations from the Pfann equation (1) becomes higher, and it increases in line with a rise in the starting concentration of tellurium. With increasing distance from the beginning of the crystal this difference became higher, as shown in Fig. 4, where the Te concentration in the GaSb melt was 4.52×10^{18} atom cm^{-3}, the N_D contribution of tellurium having always been lower than the C_c from the Pfann equation.

TABLE 3

Comparison of the theoretical values (C_c) from the Pfann equation with the measured contribution of tellurium $|(N_D - N_A) - N_U|$ in Te-doped GaSb single crystals for $x = 0.02$

Crystal number	Conc. in the melt (atom cm^{-3})	Conc. according its Pfann eqn. (1) (atom cm^{-3})	$\|(N_D - N_A) - N_U\|$ (atom cm^{-3})	Deviation (%)
GaSb-85	9.2×10^{16}	2.94×10^{16}	3.07×10^{16}	+4.4
GaSb-58	4.37×10^{17}	1.40×10^{17}	1.48×10^{17}	+5.7
GaSb-60	8.00×10^{17}	2.56×10^{17}	2.57×10^{17}	+0.4
GaSb-83	2.29×10^{18}	7.33×10^{17}	7.04×10^{17}	−0.4
GaSb-42	4.52×10^{18}	1.45×10^{18}	1.27×10^{18}	−12.4

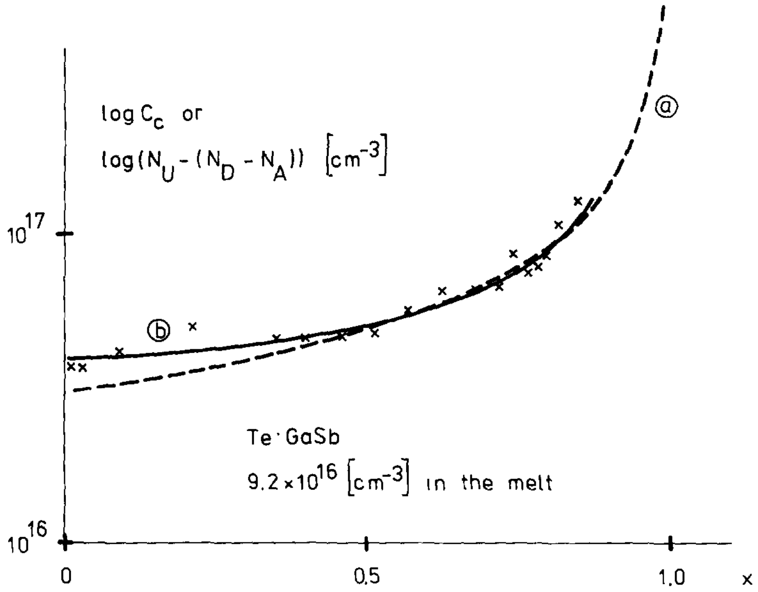

Fig. 3. The Te concentration along the growth direction in Te-doped GaSb single crystal (the Te concentration in the starting melt was 9.2×10^{16} atom cm^{-3}); x is the solidifying fraction. Curve a shows the theoretical calculation from the Pfann equation ($\log(C_c)$ versus x); curve b shows the measured Te contribution of N_D concentration ($\log(N_U - (N_D - N_A))$ versus x).

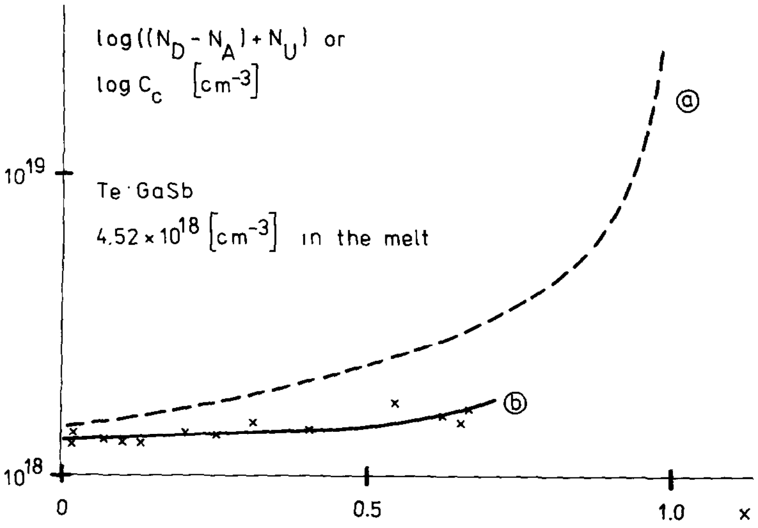

Fig. 4. The Te concentration along the growth direction in Te-doped GaSb single crystal (the Te concentration in the starting melt was 4.52×10^{18} atom cm^{-3}); x is the solidifying fraction. Curve a shows the theoretical calculation from the Pfann equation ($\log(C_c)$ versus x); curve b shows the measured Te contribution of N_D concentration ($\log((N_D - N_A) + N_U)$ versus x).

We assume that at lower Te concentrations all Te atoms are ionized and so they effectively contribute to increasing the N_D concentration. But at higher levels of Te doping some unknown mechanism seems to appear which may increase the effective ionization of tellurium. We can suppose that Te complexes occur, but our microscope studies did not show any evidence of Te precipitates. This is in agreement with measurements by Sunder et al. [10].

It is worth mentioning that we also studied the dislocation density (EPD) of these crystals. The change of EPD was not, however, found to be connected with the increment of Te concentration, and was almost identical for all the Te-doped GaSb single crystals grown by the Czochralski technique. This problem will be a subject of our subsequent study.

CONCLUSION

A series of undoped and Te-doped GaSb single crystals were grown by means of the Czochralski technique without encapsulant in a flowing hydrogen atmosphere with very low temperature gradients. It was shown that the original impurities in a starting material can influence the residual carrier concentration in the order of $\approx 10^{16}$ atom cm^{-3}. If this effect is suppressed on account of a mathematical operation, the value of the concentration of residual acceptors is $\approx 1.7 \times 10^{17}$ atom cm^{-3}. This remaining concentration can be caused by either antisite defects or crystalline nonstoichiometry [10].

The normal freeze equation [13] describes very well the N_D contribution of tellurium introduced into the GaSb single crystals under conditions such that the Te concentration in the starting melt is lower than 8.0×10^{17} atom cm^{-3}. In the case of higher levels of Te doping, the carrier concentration of tellurium donors is lower than the values calculated from the Pfann equation. This may be caused by the existence of some mechanism which decreases the effective ionization of tellurium.

We found that the normal freeze equation is especially useful in the case of a very low Te concentration, when the Te-doped single crystals always show p-type conductivity.

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