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Study of dislocation density in Te-doped GaSb single crystals grown by means of Czochralski technique

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Abstract

A series of Te-doped GaSb single crystals were grown by means of the Czochralski method without encapsulant in a hydrogen atmosphere. The possible influence of tellurium in decreasing the dislocation density was studied, but no such effect was observed because the temperature gradients in the furnace were very low, thus considerably lowering the possibility of stress creation on the solidification surface. However, it was found that the elimination of dislocations at the beginning of the growth procedure of GaSb grown in the ⟨111⟩ direction was influenced by the angle which the shoulders of the crystal included. The critical angle was determined as 38.94°. Below this value the dislocations were grown out and the dislocation density rapidly decreased in the course of crystal growth.

INTRODUCTION

Until now, GaSb single crystals have been investigated only infrequently in comparison with some other III–V compounds (such as GaAs, InP or GaP). The probable reason for this situation may be the high concentration of vacancies and anti-site defects [1] and the difficulty of mechanical surface polishing because of the limited hardness of GaSb. Wafers of GaSb are important as substrates for the growth of (GaIn)(AsSb) or (GaAl)(AsSb) layers applicable in optical communications. During the growth of layers of the GaSb substrates there are no problems with differential contraction during the cooling cycle because the expansion coefficients of the layers and the substrates are close to one another [2].

Therefore one of the main problems is the good structural quality of GaSb single crystals, which can be influenced by dislocation density. The distribution and creation of dislocations were studied in detail on various crystals, e.g. those grown by means of the Bridgman method [3, 4], the

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horizontal travelling heater method [5], the vertical gradient freeze technique [6] and LEC under different encapsulants [7–9]. However, the most suitable method for the growth of compounds with low vapour pressure of the volatile components, as represented by GaSb, seems to be the Czochralski technique without encapsulant but under a reducing ambient gas [10–13]. Some authors [7, 11, 14] found that the undoped crystals are of relatively poor quality. Doping by certain impurities can reduce the formation of dislocations as a result of higher thermal stresses which are always inherent in the Czochralski type of growth evidenced in most III–V compounds [15]. Using tellurium as a dopant, dislocation free single crystals can be formed [11]. The detailed course of dislocation formation and consequent effect of etch pit density on the dopant concentration has not been studied and correlated for GaSb crystals grown by means of the Czochralski technique without encapsulant.

The aim of our investigation was to study the origin of dislocations in undoped and Te-doped GaSb single crystals with different concentrations of tellurium. We were also interested in investigating the so-called "hardening effect" [15], which affects the quality and the etch pit density of GaSb crystals.

CRYSTAL GROWTH

The Czochralski apparatus for the growth of GaSb single crystals and the growth procedures are described in detail in previous papers [13, 16]. A polycrystalline material made by the firm Spurmetalle Freiberg (Germany) was used as the starting material for our investigation. Its purity is specified in ref. 16. Before the growth, the polycrystalline GaSb was 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 then placed in a quartz crucible. Elementary tellurium (purity 6N) was used as a dopant and added to the charge (170 g) in an amount of 4.3×10^{17}–4.5×10^{18} atoms cm^{-3}.

The crystals were grown in the ⟨111⟩ direction, i.e. the *b*-axis against the melt by applying a pulling rate of 12 mm h^{-1} and the seed rotation was varied in the range 20–25 rpm. For the suppression of oxide formation, a well purified hydrogen atmosphere was used. The flow rate of the ambient gas was kept at a value of 70 cm^3 min^{-1}.

The temperature profile was measured along the pulling direction at both the centre and the wall of the crucible (Fig. 1). It was found that a very small temperature gradient exists in the radial direction of the melt. The temperature gradients in the axial direction were also very small. Their values above the GaSb melt reached only ≈35°C cm^{-1}, which is really low in comparison with the LEC method [7], in which temperature gradients are 150°C cm^{-1} or even higher. For this reason the possibility of creation of thermal stresses was markedly decreased.

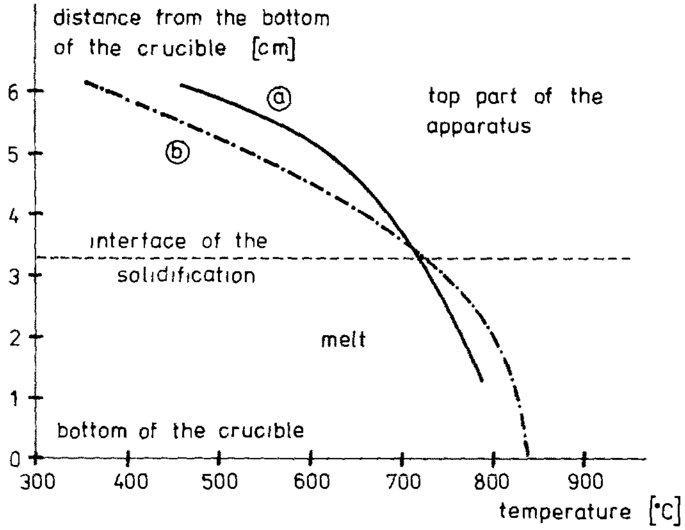

Fig. 1. Temperature distribution along the pulling direction. Curve a shows the temperature at 2 mm from the wall of the quartz crucible, and curve b that at the centre of the crucible.

RESULTS AND DISCUSSION

To observe dislocations it was necessary to use chemical etching. For the investigation of dislocations the GaSb crystals were cut along the growth direction to prepare samples ≈1 mm thick. Both faces of such wafers were mechanically polished using an alumina suspension on a thick glass plate. Afterwards the wafers were rinsed in water, in acetone and finally in distilled water several times.

Such prepared wafers were etched for 2 min under continuous stirring in a solution of 45% KOH in water. Then the samples were rinsed very quickly in distilled water and immediately etched in an acid solution (1 part HF + 9 parts HNO_3 + 20 parts CH_3COOH) for 1 min. After this operation the wafers were immediately put into a solution of 5% of Br_2 in CH_3OH, and intermittent stirring was maintained for about 5 min. After this final etching they were repeatedly rinsed in C_2H_5OH and finally in CH_3OH. The whole etching procedure was performed at room temperature.

The dislocation etch pits were conventionally studied by means of a metallographic microscope at ×50 magnification. The dislocation density was observed on the Ga side of the wafer only, and had a triangular shape corresponding to the crystal symmetry. Etch pits on the Sb side did not exhibit good quality.

The etched sample was divided into nine sections and etch pits were counted in five positions on every section [13]. The dislocation density was calculated from the arithmetic average over all sections.

We found that the dislocation density is not spread uniformly over the surface. The highest concentration of etch pits was regularly found near the edge of the wafers, but some places without dislocations were also observed. The average dislocation density decreased with growth distance from the beginning to the end of the crystal. This fact was already noted in several papers [5–7, 17] but was explained differently.

(a) Dislocation pairs of opposite Burgers vectors can annihilate each other [15], but this effect works only when the dislocation density is very high (over 10^5 cm^{-2}) [18]. However, the concentration of etch pit density in our crystals were less than 10^4 cm^{-2};
(b) if a solidification interface is convex towards the liquid, then dislocations are eliminated by emerging out of the crystal [7, 17]. Our solidification interface, however, was almost flat;
(c) if the crystal is grown in the ⟨111⟩ direction, then dislocations are eliminated during solidification on the lateral surfaces owing to glide phenomena [6].

This third mechanism is the most plausible in our case, but the starting angle of the crystal from the growth axis would have to be lower than a complement of the angle between the ⟨111⟩ growth plane and the other ⟨111⟩ planes (70.53°) to a right angle — that means 19.47°. If the shoulders of the crystal include an angle of less than 38.94° we can assume that the dislocations will be grown out of the crystal and only random dislocations will remain. These would arise because of either impurities or local temperature fluctuations, which can cause the critical resolved shear stress (CRSS) threshold to be exceeded.

We prepared three undoped GaSb single crystals with a different starting angle of the crystal shoulders. The value for the first crystal was 23.8°, that for the second was 14.2° and the angle of the third was kept in the beginning at a value of 46.8°. After 15 mm of growth length the crystal stopped growing so fast, so that the value of the angle decreased and was further kept at a lower value (29%) during the remaining growth (20 mm).

Figure 2 shows the dislocation density along the growth direction of the GaSb crystals. In the case of the crystals represented by curves a and c, the starting angles are lower than the above mentioned values (38.94°) and the concentration of etch pits decreases smoothly from the beginning to the end of the crystals. However, the dislocation density profile b shows a different shape. In the first portion, where the starting angle was higher than 38.94°, the etch pit density stays almost the same or increases slightly. If the angle between the shoulders of the crystal decreases below this value the concentration of dislocations starts to reduce. It is noted that the seed used was the same in all cases and we observed only three etch pits on its surface. The seed had the dimensions 4 mm × 4 mm, i.e. the dislocation density on its side against the melt was

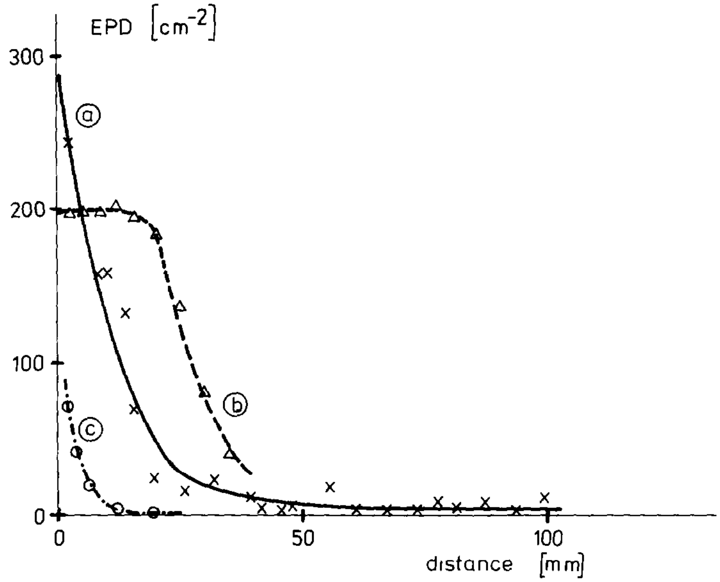

Fig. 2. Dislocation density along the growth direction ⟨111⟩ of the GaSb single crystals. Curves show the dislocation profiles for different starting angles of the crystal shoulders: a, for an angle of 23.8°; b, first 15 mm with an angle of 46.8° and then 20 mm with an angle of 29°; c, for an angle of 14.2°.

only 19 cm^{-2}. The necking procedure was performed identically for all grown undoped crystals.

Hence it follows that the angle of the shoulders near the necking of a crystal can influence the elimination of dislocations in GaSb crystals grown in the ⟨111⟩ direction. If the starting angle is lower than 38.94° the concentration of dislocations decreases, and it is possible to obtain a dislocation-free crystal.

The profiles of dislocation density in Te-doped GaSb single crystals with different levels of doping show the same shape. The starting angles were maintained at the almost identical values of about 24°. The dislocation density was measured in four Te-doped GaSb crystals with different concentrations of tellurium. From each crystal the middle portion was selected, where the concentration of etch pits was almost unchanged. The average dislocation density was calculated for wafers from this part. The results are shown in Table 1. For comparison we added the etch pit density (EPD) from the undoped GaSb single crystal, where the dislocation density is computed in the same way.

The etch pit density of the Te-doped GaSb crystals is almost the same for all Te concentrations used and comparable with that for the undoped crystal. Therefore we cannot detect the dependence of EPD on the concentration of tellurium. The small difference of EPD among the measured crystals can be caused by the origination of random dislocations

TABLE 1

Average dislocation density (EPD) and root-mean-square deviation (RMS) from the middle portion of undoped and Te-doped GaSb single crystals

Concentration of tellurium in the melt (atoms cm^{-3})	EPD (cm^{-2})	RMS (cm^{-2})
Undoped	15	18
4.3×10^{17}	129	35
8.0×10^{17}	62	30
2.3×10^{18}	139	44
4.5×10^{18}	4	10

or temperature fluctuation during the growth. In the case of low temperature gradients during the crystal growth, the so-called "hardening effect" would have either no effect or only a slight one. The undoped GaSb shows a very low level of dislocation density in the whole crystal, and therefore it is not possible to identify the influence of dopant as a decrement of EPD.

It is hardly necessary to state that the necking procedure was performed very carefully. After contact with the melt, the seed was immersed in the melt to about 5 mm and then pulled to a length of 10 mm with an unchanged diameter (a so-called "new neck"). After this operation the neck started to enlarge under the above mentioned angles. In order to

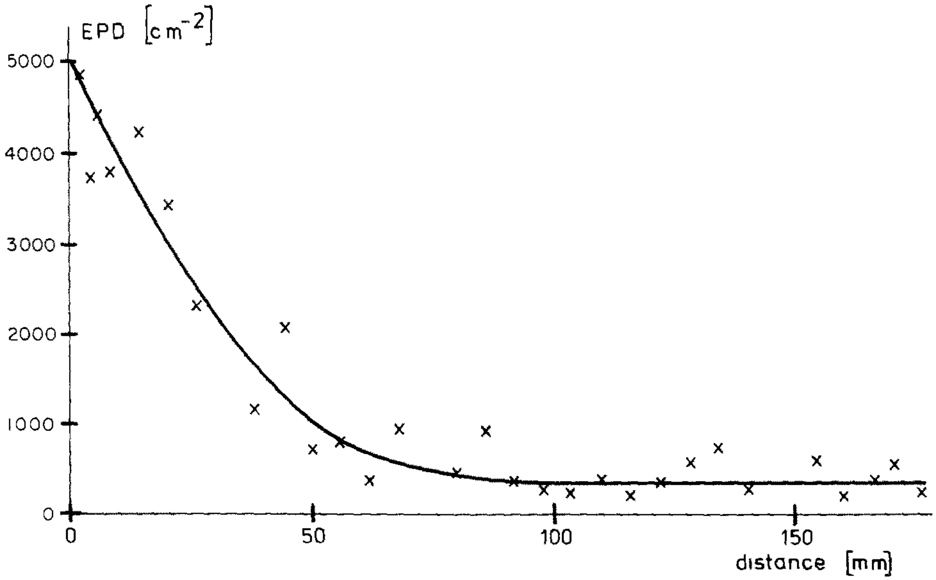

Fig. 3. Dislocation density along the growth direction ⟨111⟩ of a GaSb single crystal grown without melt-back of the seed and without preparing a so-called "new neck".

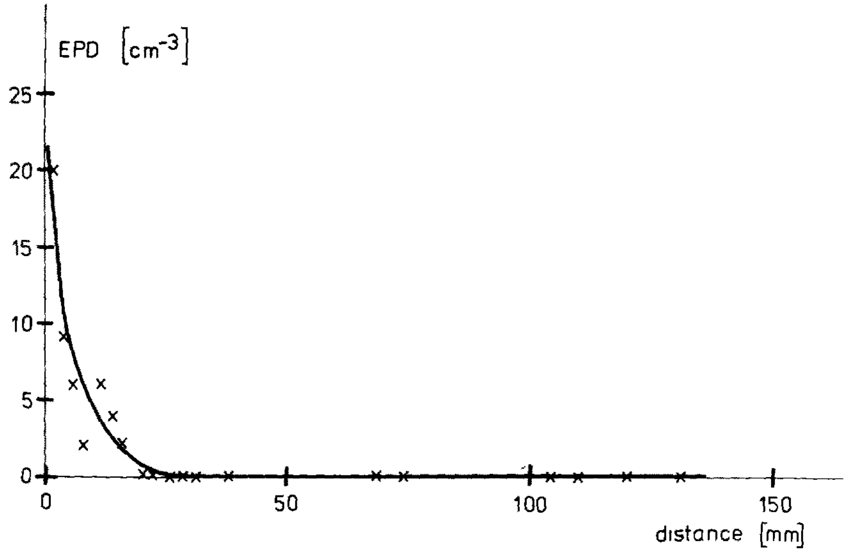

Fig. 4. Dislocation density along the growth direction ⟨111⟩ of the GaSb single crystal grown with 5 mm melt-back of the seed and with preparation of a 10 mm long so-called "new neck".

verify whether our procedure was right, we performed the crystal growth without melt-back and pulling the long neck. The starting concentration of dislocations was very high (Fig. 3) in comparison with the crystals grown by the above mentioned procedure (Fig. 4), where the EPD can decrease to zero after several centimetres of growth, while during fast necking the concentration of dislocations decreases from a value of 5000 cm^{-2} down to a density of $\approx 10^2$ cm^{-2}.

CONCLUSION

Undoped and Te-doped GaSb single crystals grown in the ⟨111⟩ direction by means of the Czochralski technique without encapsulant and in a flowing hydrogen atmosphere were studied regarding the influence of tellurium as a dopant on the dislocation density. It was found that the temperature gradients in this apparatus were very low ($\approx$30–40°C cm^{-1} in the solidification interface). This fact makes it possible to grow undoped single crystals with levels of dislocation density approaching zero. The doping of tellurium in GaSb could not essentially be detected as a decrement of EPD, i.e. the "hardening effect" did not appear.

It was shown that the dislocation density rapidly decreased along the crystal, and in many cases (Te-doped and also undoped GaSb) it reached a value of zero in the end part of the crystal. However, the starting concentration of dislocations depends on good necking procedure and on the angle which the shoulders of the crystal include. We found that this angle can influence the elimination of dislocations in GaSb grown in the ⟨111⟩ direction. If its value should be lower than 38.94° the dislocations would grow out unless they remain inside the crystal. This indication is in good agreement with ref. 6 because, if the angle was 46.8°, the starting concentration of dislocations was the same during the growth of a crystal. If the value of the angle was lowered to 29° the density started to decrease rapidly, and after about 4 cm the EPD was $\approx 10^1$ cm^{-2}.

Finally, our results show that the influence of tellurium doping will be detectable in crystal growth where the temperature gradients in the furnace are high and the glide threshold can be exceeded.

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