CONF-9705119--

BULK GROWTH OF GaSb and Ga_{1-x}In_xSb

G. Charache, P. S. Dutta, et. al.

RECEIVED
MAR 04 1999
OSTI

May 1997

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States, nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

KAPL ATOMIC POWER LABORATORY

SCHENECTADY, NEW YORK 10701

Operated for the U. S. Department of Energy
by KAPL, Inc. a Lockheed Martin company

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Bulk growth of GaSb and $\text{Ga}_{1-x}\text{In}_x\text{Sb}$

P.S. Dutta^{*}, A.G. Ostrogorsky^{*} and R.J. Gutmann^{**}

Center for Integrated Electronics and Electronics Manufacturing

^{*}Department of Mechanical Engineering, Aeronautical Engineering and Mechanics

^{**}Department of Electrical, Computer and Systems Engineering

Rensselaer Polytechnic Institute, Troy, New York 12180

Abstract. Synthesis and growth of bulk GaSb single crystals and GaInSb polycrystals have been carried out by the vertical Bridgman technique, with a baffle immersed in the melt and by complete encapsulation of the melt by low melting temperature alkali halides or oxides. The critical roles of the baffle and the encapsulation are discussed. Efforts in obtaining device grade GaSb with superior structural and electrical properties and compositionally homogeneous GaInSb are described, emphasizing the key steps in the growth cycle developed to obtain good crystalline quality.

INTRODUCTION

GaSb and InGaSb have been demonstrated to be suitable choices for high efficiency thermophotovoltaic (TPV) cells [1]. At present, GaSb technology is in its infancy, and considerable research is needed prior to large scale device manufacturing. However, advancement in crystal growth of GaSb and InGaSb offers the possibility of improved performance and yield of TPV devices, as well as other low band gap devices.

Compared to other III-V compounds such as GaAs, InP, GaN, GaP and InAs, the synthesis and growth of GaSb is much simpler [2]. In particular, Sb has a low vapor pressure and is less toxic than As or P, thus eliminating the complication of using furnaces enclosed in high pressure chambers. Moreover, the synthesis and growth temperature of GaSb (712°C) is much lower than that of the other compounds. The thermo-physical properties of molten GaSb, the high stacking fault energy (highest amongst III-V compounds), and the high critical resolved shear stress (CRSS) indicate that the growth of high structural quality bulk material should be achievable. All of these factors indicate that low cost growth of such material should be quite feasible.

However, GaSb and related alloys have high native defect concentrations which are electrically and optically active, and pose problems in device fabrication. A review of the vast literature on other III-V compounds indicates that the lack of a commercial market for GaSb based devices has resulted in insufficient research for a consistent understanding of these defects, although recent work is very promising [3]. The present investigation is a part of the on-going development program for the growth of antimonide based boules for TPV cells [4].

A combination of several advanced concepts of bulk crystal growth is reported. Each concept has been separately proven to produce high quality materials. The three principal features are summarized below:

- (i) The experimental growth setup is a state-of-art multi-zone, computer controlled Mellen furnace, custom built for crystal growth in an industrial environment. This setup allows precise control of the temperature profile during boule growth.
- (ii) The vertical Bridgman technique, which has been found to result in lower dislocation and defect density when compared to the traditional Czochralski (CZ) method, has been adopted. A few technical problems have been encountered during the growth of GaSb with the CZ technique, especially during seeding. The formation of Ga_2O_3 scum on the melt during synthesis impedes seeding of the charge [5]. The reduction kinetics of the scum is very slow at the low growth temperature of GaSb (712°C); therefore, the scum is difficult to remove from the top of the melt [6]. Similarly, due to the high viscosity of B_2O_3 at the melting temperature of GaSb (conventionally used for encapsulation during CZ growth of III-V materials), seeding becomes problematic [7].
- (iii) Liquid encapsulation with low melting point salts of alkali halides is used to relieve the stress from the walls of the crucible during growth, and at the same time remains inert with respect to the melt and crystal [8]. The use of a baffle in the melt, which is novel for compound synthesis and subsequent growth of the crystal, is one of the highlights of previous experiments [9]. The submerged baffle has several important roles. Compound synthesis is done in open ampoules (under inert atmosphere) in less than one hour compared to tens of hours using conventional techniques; therefore, impurity incorporation in the melt is reduced. The incorporation of a baffle during the growth encompasses the advantages of the vertical gradient freeze technique, double crucible Czochralski (CZ) method, and traveling heater method (or float zone technique). Ultimately, a low radial temperature gradient, introduction of compositional uniform melt at the S-L interface (as in the case of the double crucible CZ technique), and a small melt depth over the solid-liquid (S-L) interface with low natural convection (diffusive controlled growth) are anticipated. The resultant boules should have lower dislocation (or defect) density and more uniform impurity distribution (or solute incorporation in the crystal). These results have been demonstrated in the growth of InSb and Ge [10,11], and are demonstrated in our present work on undoped and Te- doped GaSb and InGaSb.

From the above mentioned summary, it can be ascertained that the preparation techniques adopted should result in higher quality material and should be easier to adopt for production. The key results obtained using these growth concepts are reported here.

BOULE GROWTH PROCEDURES

Charge and crucible preparation

Growth of GaSb (undoped and Te-doped) has been carried out mainly in silica crucibles with oriented seeds along $\langle 111 \rangle_B$ and $\langle 100 \rangle$, with a few experiments in pyrolytic boron nitride (pBN) crucibles. The liquid encapsulants used during the experiments were: LiCl:KCl eutectic (58% : 42%) salt [8], B_2O_3 and Sb_2O_3 . These encapsulants were of high purity commercial grade with the LiCl:KCl eutectic mixture prepared in-house. The growth of the InGaSb crystals was carried out without a seed in flat-bottom silica crucibles. The starting materials (In, Ga, and Sb) were of 6N purity which were not chemically treated before synthesis to reduce the chances of enhanced oxidation on the freshly etched surfaces of the elements. The oxidized surfaces form a layer of scum on the melt and lead to sticking of the charge to the ampoule walls. By using untreated starting materials, the formation of scum can be reduced. The silica ampoules and silica baffles or the pBN crucible were cleaned in organic solvents followed by acid treatments and de-ionized (DI) water wash. The ampoules and baffle were thoroughly dried with nitrogen and then with a hot plate.

The starting materials were placed in the crucible which was then loaded in the furnace. For synthesis, flat bottom crucibles were used, while for seeded growth narrow seed regions were used. Since the diameter of the seed region is usually non-uniform along its length, this region was drilled with a diamond coated steel rod dipped in methanol. The seeds were drilled from single crystal boules using a diamond coated core drill of steel. The prepared seed was then etched in CP4 etchant to fit the seed cross-section of the ampoule. In experiments where a pre-synthesized charge was used, the charge was degreased thoroughly in organic solvents and etched in CP4 etchant to obtain a mirror-like surface. Care was taken to avoid any unreacted or oxidized portions of the charge after etching by using DI water to stop the vigorous reaction. The charge was then thoroughly washed in DI water and methanol with ultrasonic vibrations. The charge was dried using nitrogen followed by heating.

Synthesis and growth sequences

After loading the charge in the furnace, a few grams of the encapsulant were inserted in the ampoule and the growth chamber was immediately evacuated to less than 50 mTorr. The encapsulants are highly hygroscopic in nature and after absorption of moisture they stick non-uniformly to the quartz at high temperature. This process results in undesirable sticking of the melt to the ampoule. The salts were preserved under vacuum in dessicators and the exposure times during insertion in the ampoule were kept extremely short. To insure a moisture-free encapsulant, a high temperature baking in vacuum was carried out prior to growth. The synthesis and growth cycle is depicted in Fig. 1.

After evacuation to below 50 milli-Torr, the growth chamber was flushed with argon several times to remove any residual oxygen. The furnace was then heated at a rate of 100°C/hr to around 300°C , which was significantly below the melting temperature of the encapsulants. This

is important in order to avoid any evaporation of the encapsulant due to melting. The pre-growth baking was carried out for a period of 10 - 12 hours under vacuum. After the baking, the furnace was filled with 1 atm of argon and heated to around 20-30°C above the melting temperature of GaSb (712°C). The synthesis was carried out by vertically moving the baffle (up and down) in the ampoule for a period of 30-40 minutes. The mixing was also done while using a pre-synthesized charge to achieve a uniformly mixed melt.

Fig. 1. Temperature versus time plot for a typical synthesis and growth cycle.

At the end of the synthesis cycle, the temperature profile of the furnace was adjusted to a typical Bridgman profile (shown in Fig. 2). The baffle was placed 1 cm away from the solid-liquid interface and the ampoule was lowered at a constant rate. For the seeded experiments, a small portion of the seed is re-melted before solidification. The seeding procedure was optimized with respect to the furnace temperature setting and position, and seeding could be repeatedly carried out without the danger of melting the complete seed. During the solidification of the charge, the baffle remained stationary while the ampoule translated along the temperature gradient of the furnace. The distance between the baffle and the S-L interface remained constant during the entire growth cycle, as experimentally verified. The translational rate of the crucible was 3.3 mm/hr in all of the experiments. After the completion of solidification, the furnace was cooled down slowly to room temperature.

The pre-synthesis baking was found to be critical for obtaining good quality crystals. In the absence of this step, the salt encapsulant turned yellowish and stuck to the charge and the crucible. The salt encapsulant was removed by hot water or methanol after the growth. However, a moisture containing salt exposed to high temperature was difficult to wash off.

Fig. 2. Experimental set up for synthesis and crystal growth along with the temperature profile of the furnace.

RESULTS AND DISCUSSION

Growth of GaSb

The motivation for the growth experiments with GaSb was to obtain low dislocation density and twin free crystals with uniform doping and superior electrical properties. The diameter of the crystals grown ranged from 32 to 51mm with length of 70 to 80 mm. Crystals with low dislocation density were obtained by using encapsulation and low temperature gradients (10-15°C/cm) near the S-L interface. Uniform doping density is obtained through the use of the baffle. However, the appearance of twins in GaSb presents a significant problem, because at present the mechanism of twin formation is not well understood. Several factors, including: (1) temperature fluctuation in the melt, (2) crystallographic orientation, and (3) sharp temperature gradient normal to the ampoule wall due to high conducting crucible support, may give rise to twins during the growth, as in the case of other III-V compounds like InP [12]. The third factor has been found to be dominant during GaSb growth, since twinning usually occurs at the junction of the seed-shoulder region of the conical ampoule. Twinning is also found to be dominant along certain crystallographic directions like $\langle 111 \rangle_A$ or $\langle 100 \rangle$ as compared to $\langle 111 \rangle_B$ [13,14]. The twins drastically reduce the yield of the crystals which otherwise show single grain nature.

Fig. 3. Crucible support designs employed in our work. (a) twin formed at the seed-shoulder junction, (b) no twinning occurred.

Through extensive study, the shape of the ampoule and the crucible support system were optimized to obtain twin free crystals. By increasing the conical angle of the ampoule and by preventing the shoulder of the ampoule to touch the graphite crucible support, as shown in Fig. 3b, the formation of twins could be avoided in the cone region. The configuration shown in Fig. 3a was found to form twins at the junction between the seed and shoulder regions. A systematic difference could not be seen in the appearance of twins in growth along the $\langle 100 \rangle$ and $\langle 111 \rangle$ B directions.

The best crystals grown with proper encapsulation exhibited uniformly distributed dislocation densities between 500 and 1000 cm^{-2} . Crystals grown with encapsulation sticking to the quartz ampoule exhibited dislocation density about one order of magnitude higher, i.e., approximately 5000 cm^{-2} . The pBN grown crystals with B_2O_3 encapsulation had a higher dislocation density than those grown with alkali halide salt, but lower than those with sticking problems [15]. The crystal grown with Sb_2O_3 encapsulation was found to stick to the quartz in a glassy-like matrix, and could not be extracted without breaking. The crystal had several areas of Sb inclusions, probably diffusing from the decomposed encapsulation.

The Hall mobility, carrier concentration and resistivity of undoped p-type and Te doped n-type (which are indicative of the crystalline quality) are listed in Table I. The electrical properties of the grown wafers are comparable, or in certain cases superior, to those available from commercial suppliers of GaSb.

Table I. Hall mobility, carrier concentration and resistivity for p- and n- GaSb

Sample specification	T (K)	type	resistivity ($\Omega\text{-cm}$)	carrier concentration (cm^{-3})	mobility ($\text{cm}^2/\text{V.s}$)
undoped #17	300	p	0.02	1.90×10^{17}	505
undoped #17	77	p	0.05	1.05×10^{17}	1275
undoped #12	300	p	0.05	2.38×10^{17}	500
undoped #12	77	p	0.09	4.10×10^{16}	1575
Te-doped #19	300	n	0.0005	6.28×10^{18}	1876
Te-doped #19	77	n	0.0001	6.81×10^{18}	6281

Growth of InGaSb

Growth of InGaSb was carried out in flat bottom crucibles, in order to obtain a compositionally homogeneous material along the radial and axial directions. Once this objective is achieved, the single crystals are expected to be grown by using GaSb seeds. The effect of the baffle in the melt and its rotation, or oscillation, during growth has been found to improve the homogeneity of Ga- doped Ge [10,11]. The same is expected to be true in InGaSb where InSb is rejected at the S-L interface during growth of InGaSb, resulting in a non-uniform axial profile of indium in the grown crystal.

Fig. 4. Axial profiles of indium in $\text{In}_x\text{Ga}_{1-x}\text{Sb}$. (a) without baffle, (b) with baffle and (c) with baffle rotation. The initial uniform concentration of indium (x) in the melt is 0.03. Note that the scales of x- and y- axes are different in the three plots.

The role of the baffle on the spatial composition of $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ crystals can be seen in Fig. 4. The initial homogenized concentration of indium (x) in the melt was 0.03. The axial indium distribution in a crystal grown without the baffle is shown in Fig. 4(a). The indium profile in the grown crystal clearly shows the dominance of convective conditions during growth. The presence of a baffle (Fig. 4b) gives rise to an initial transient due to build-up of the solute boundary layer at the bottom of the baffle. However, as the concentration of indium in the boundary layer rises, constitutional super-cooling occurs and a sharp increase in the indium concentration is observed. This super-cooling is repeated several times during the whole growth cycle, which leads to the observed wavy shape of the indium profile. The oscillatory rotation of the baffle (Fig. 4c) gives the most homogeneous crystal. Moreover, the indium incorporation in the crystal is higher than in the previous two cases.

The role of encapsulation during synthesis has been found to be significant. Sticking of In, or its oxide, to the silica and subsequent cracking of ampoule has been a major problem reported by other workers [16]. An alkali salt avoids the sticking of the In to the quartz; hence, a homogeneous mixture can be prepared. Imperfections in bulk InGaSb crystals caused by cracks generated due to chemical misfit in the ternary materials [17] must be solved before highest quality crystals can be anticipated.

CONCLUSION

The critical issues in the bulk growth of GaSb and InGaSb were discussed describing a particularly attractive approach adopted in this program. GaSb boules with electrical properties comparable to or better than commercial crystals have been obtained. Growth of twin-free $\langle 100 \rangle$ GaSb single crystals is essential for device-quality material. Cracks encountered in ternary crystals are a key drawback for InGaSb boules, although enhanced mixing and heavy impurity doping are promising approaches.

ACKNOWLEDGMENTS

The authors wish to acknowledge Dr. Thierry Duffar and Dr. Eric Monberg for providing invaluable scientific information and discussions. Thanks are due to Dr. David Wark for the EPMA measurements. The growth equipment used in the present work was provided by the A T & T Bell Laboratories at Murray Hill, New Jersey.

REFERENCES

1. Benner, J.P., Coutts, T.J. and Ginley, D.S., Editors, *The Second NREL Conference on Thermophotovoltaic Generation of Electricity*, AIP Conference Proceedings 358, AIP Press, 1996.
2. Sunder, W.A., Barns, R.L., Kometani, T.Y., Parsey, Jr., J.M., and Laudise, R.A., *J. Cryst. Growth* **78**, 9 (1986).
3. Dutta, P.S., Bhat, H.L. and Kumar, Vikram., "The physics and technology of gallium antimonide: an emerging optoelectronic material" *to be published in Applied Physics Reviews, J. Appl. Phys.* **89** (9), 1 May 1997.
4. Charache, G.W., DePoy, D.M., Baldasaro, P.F., and Campbell, B.C., "Thermovoltaic devices utilizing a back surface reflector for spectral control" *The Second NREL Conference on Thermophotovoltaic Generation of Electricity*, AIP Conference Proceedings 358, AIP Press, 1996, pp. 339.
5. McAfee, Jr., K.B., Gay, D.M., Hozack, R.S., Laudise, R.A., Schwartz, G. and Sunder, W.A., *J. Cryst. Growth* **76**, 263 (1986).
6. Cockayne, B., Steward, V.M., Brown, G.T., MacEwan, V.R. and Young, M.I., *J. Cryst. Growth* **58**, 267 (1982).
7. Uemura, C. and Katsui, A., *Jpn. J. Appl. Phys.* **19**, L318 (1980).
8. T. Duffar, Personal Communication, 1995.
9. Ostrogorsky, A.G., *J. Cryst. Growth* **104**, 233 (1990).
10. Ostrogorsky, A.G. and Muller, G., *J. Cryst. Growth* **137**, 64 (1994).
11. Meyer, S. and Ostrogorsky, A.G., *J. Cryst. Growth* **171**, 566 (1997).
12. Monberg, E., "Bridgman and related techniques", Chapter 2 in the *Handbook of Crystal Growth, Vol. 2a, Editor, Hurle, D.T.J.*, North Holland/Elsevier, 1994, pp. 51.
13. Katsui, A. and Uemura, C., *Jpn. J. Appl. Phys.* **21**, 1106 (1982).
14. Moravec, F., Sestakova, V., Stepanek, B. and Charvat, V., *Cryst. Res. Technol.*, **24**, 275 (1989).
15. Koh, H.J. and Ostrogorsky, A.G., (unpublished work).
16. Marin, C., Dutta, P.S., Dieguez, E., Dusserre, P. and Duffar, T., *J. Cryst. Growth* **174**, (1997).
17. Garandet, J.P., Duffar, T. and Favier, J.J., *J. Cryst. Growth* **106**, 426 (1990).