LM-03K034
April 14, 2003

Reduction of Micro-Cracks in Large Diameter $In_xGa_{1-x}Sb$ Bulk Crystals

Juliet Vogel and Partha S. Dutta

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.

Reduction of Micro-Cracks in Large Diameter $In_xGa_{1-x}Sb$ Bulk Crystals

Juliet Vogel[*] and Partha S. Dutta[**]
[*]Department of Engineering Science
[**]Department of Electrical, Computer and Systems Engineering
Rensselaer Polytechnic Institute, 110 8th Street
Troy, New York 12180, USA

ABSTRACT

The ternary alloy, $In_xGa_{1-x}Sb$, is a compound semiconductor of tunable bandgap in the range of 0.18 - 0.72 eV, making it useful for infrared range optoelectronic devices. Utilizing a unique system based upon vertical Bridgman technique, large diameter (50 millimeter) $In_xGa_{1-x}Sb$ polycrystals of composition ranging in x from 0.015 to 0.988 were grown. Methods of mixing the melt during solidification, including the accelerated crucible rotation technique (ACRT), have been used in conjunction with optimization of the furnace temperature gradient profile to significantly reduce micro-cracking in the crystal boules while accelerating the growth rate from less than a millimeter per hour to three millimeters per hour. In this paper, the experimental system and crystal growth parameters for a set of ternary experiments will be detailed. Scanning probe microscopy (SEM) images of vertical cross-sections of $In_{0.15}Ga_{0.85}Sb$ samples show a 95.8 percent reduction in micro-cracking resulting from specific melt mixing schemes. The mechanism for micro-crack removal during bulk alloy growth will be discussed briefly.

INTRODUCTION

Bulk crystal growth followed by impurity diffusion to form p-n junctions, is a well established economical process for low cost, large volume devices using diffused Ge or binary III-V and II-VI compounds. However, similar research and development on bulk ternary and quaternary compounds has not been as successful, primarily due to experimental difficulties in growing spatially-homogeneous multi-component semiconductor alloys. The large separation between the liquidus and solidus phases leads to compositional segregation which, coupled with differences in the lattice parameters and thermal expansion coefficients of the constituent binaries, causes excessive strain in the solid crystal lattice, often resulting in mechanical cracking of the crystals.[1] However, evidence has shown that utilizing mixing prior to solidification and high temperature gradients during growth can reduce this mechanical cracking and improve crystalline quality.[11,3] Also, using the accelerated crucible rotation technique (ACRT) developed by Scheel and Schultz-Dubois in 1971[4,5], improvements in the physical quality have been obtained for binary compounds and electro-optic crystals.[2,6] Combining these techniques, the effect on the density of micro-cracks in $In_xGa_{1-x}Sb$ crystals synthesized by the vertical Bridgman technique has been studied.

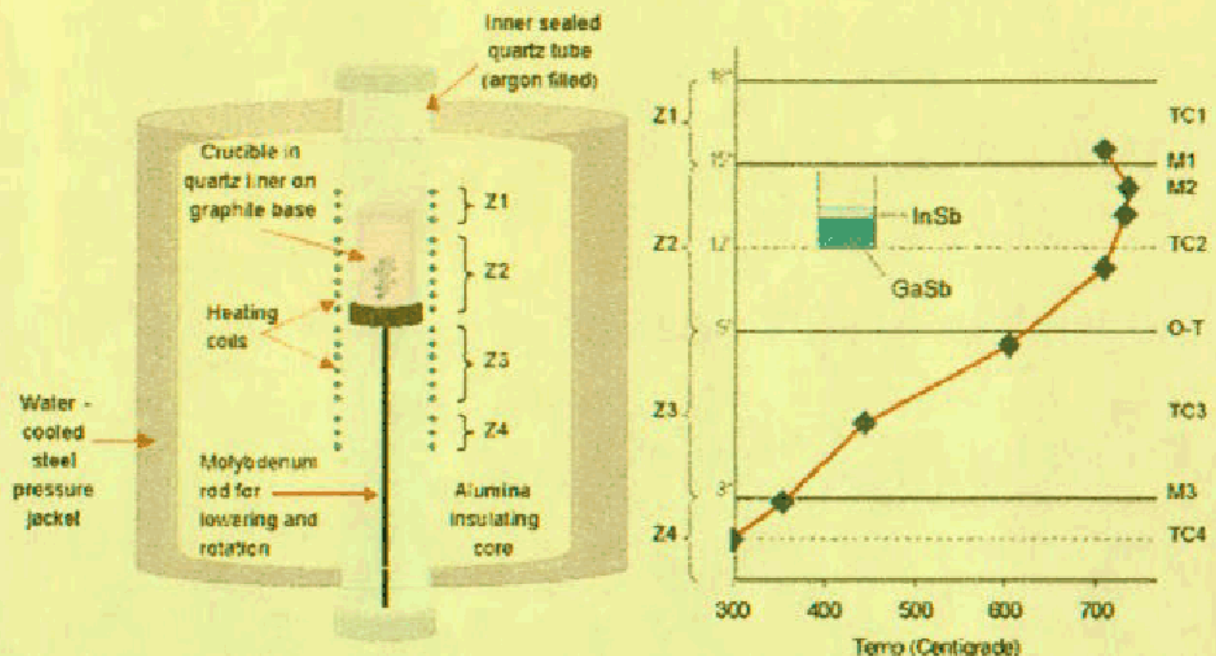

Figure 1. Four-zone vertical Bridgman furnace used to synthesize $In_xGa_{1-x}Sb$ material (left), shown with the temperature gradient used in these experiments plotted against vertical drop in the furnace (right). "TC" indicators are temperature control thermocouples, while "M" and "O/T" indicate independent temperature monitors.

EXPERIMENTAL DETAILS

Fifty millimeter diameter boules of $In_xGa_{1-x}Sb$ have been synthesized using vertical Bridgman techniques (VBT)[7,8] in conjunction with accelerated crucible rotation techniques (ACRT). This paper compares two experiments to evaluate the effect of melt mixing. Both ternary samples of $In_xGa_{1-x}Sb$ were synthesized from gallium antimonide (GaSb) and indium antimonide (InSb), which in turn was synthesized in-house from 4N or greater purity commercially-obtained indium, gallium, and antimony. Ternary boules were grown at a temperature gradient of 5.1 degrees Celsius per hour, calculated from a lowering rate of 3 millimeter per hour on a hot zone which had a near-linear temperature gradient ranging from 710 to 445 degrees Celsius as shown in Figure 1 on the right. This furnace is capable of maintaining temperature to plus or minus 0.2 degrees Celsius.

Both experiments were performed under identical conditions except for the addition of ACRT rotation during solidification for one sample. Prior to lowering and solidification, the samples were held at temperature for six hours and then rotated for six hours to fully mix the constituents prior to growth. This eliminated the need to wait for the melt components to fully incorporate by diffusion, a process which may take days or weeks.[9,10] After this six-hour rotational mixing, the three millimeter per hour lowering was started. For one of the experiments, ACRT was used to rotate the crucible during solidification. The other experiment was performed without any rotation. The ACRT scheme used was a clockwise rotation at 100 rotations per minute (rpm) for

ten seconds, pausing for two seconds, and then rotating counter-clockwise for ten seconds also at 100 rpm. A schematic of the temperature profile is shown in Figure 2.

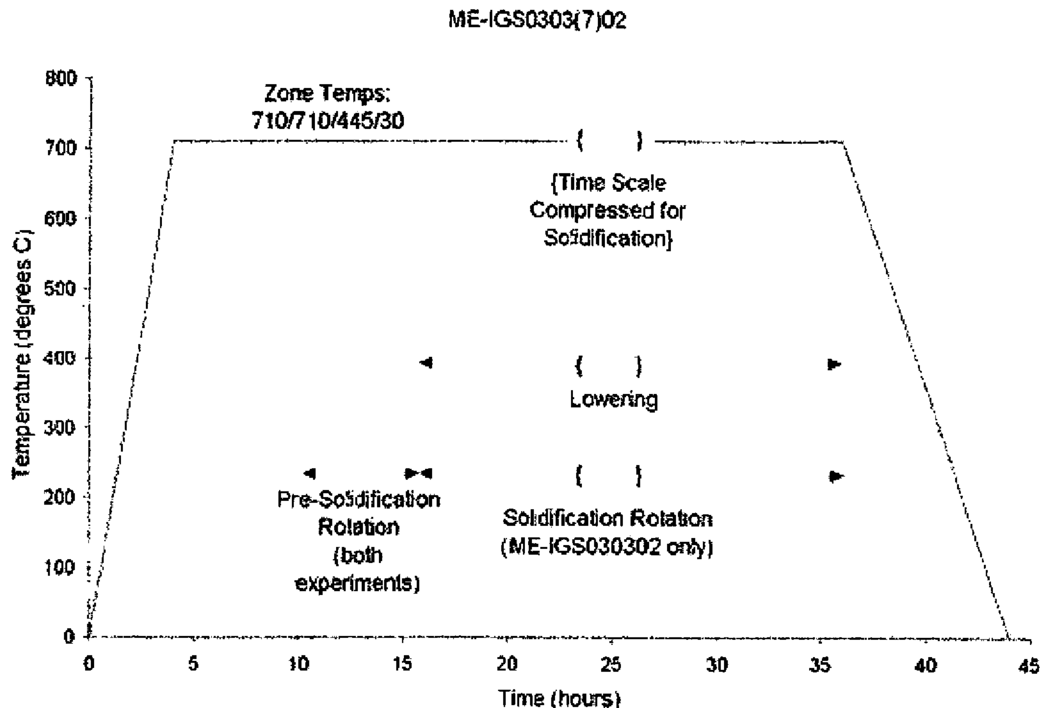

Figure 2. Schematic of the temperature plotted against time for $In_xGa_{1-x}Sb$ synthesis. Heating, cooling and relative rotation times are shown. Note that the time scale is compressed for the full lowering time. The actual lowering time for both experiments was 53.5 hours.

After growth , both samples were sliced in the vertical direction (in the direction of solidification) with a South Bay Technologies diamond wheel saw (Model 660). These samples were degreased, lapped and polished using conventional semiconductor techniques, then mounted on aluminum chucks. The samples then underwent electron probe microscopic analysis (EPMA) using a Jeol 733 Superprobe. Wavelength-dispersive spectrometry was performed to independently detect indium, gallium, and antimony in samples. The data was adjusted using Heinrich ZAF correction. SEM images of the samples at select locations were made at this time.

DISCUSSION

Visual inspection of the vertical cross-sections revealed many interesting features of these samples. Both samples exhibited some thermal cracking, seen in Figure 3 as large cracks crossing grain-boundaries. $In_xGa_{1-x}Sb$, being brittle like most semiconductors, cannot absorb the expansive stress caused by the different rates of expansion in layers of different temperature, thus large cracks form in the direction of solidification. This phenomena may be reduced by lowering the temperature gradient used during solidification and post-solidification cooling.

Some material inclusions were also visible in the vertical cross-sections, particularly in the lower or "first-to-freeze" regions of the crystal. This indicated incomplete mixing before and during solidification. This may be reduced by increasing the pre-solidification rotation step from six to twelve hours. It is worth noting that the visible inclusions were remarkably reduced in the ACRT sample, which exhibited few indium inclusions and no visible antimony inclusions.

Of particular interest was any possible decrease in "micro-cracks" due to the use of ACRT. EPMA compositional data along with SEM images was acquired at points across samples. Figures 4 & 5 show SEM images taken at equivalent areas in the center of the samples. The measured composition at these locations was $In_{0.16}Ga_{0.84}Sb$ for the unrotated sample and $In_{0.15}Ga_{0.85}Sb$ for the sample grown with ACRT during solidification.

Figure 4 shows a 2.25 by 2.75 millimeter SEM scan of the experiment performed without ACRT during solidification. This picture shows smaller cracks that begin or end at grain boundaries, indicating their formation during the solidification process. These "micro-cracks" result from the differences in thermal expansion coefficients between areas of different composition (slight changes in the value of x in $In_xGa_{1-x}Sb$.) In Figure 4, numerous micro-cracks are visible, calculated at an average of 40.0 cracks per square centimeter.

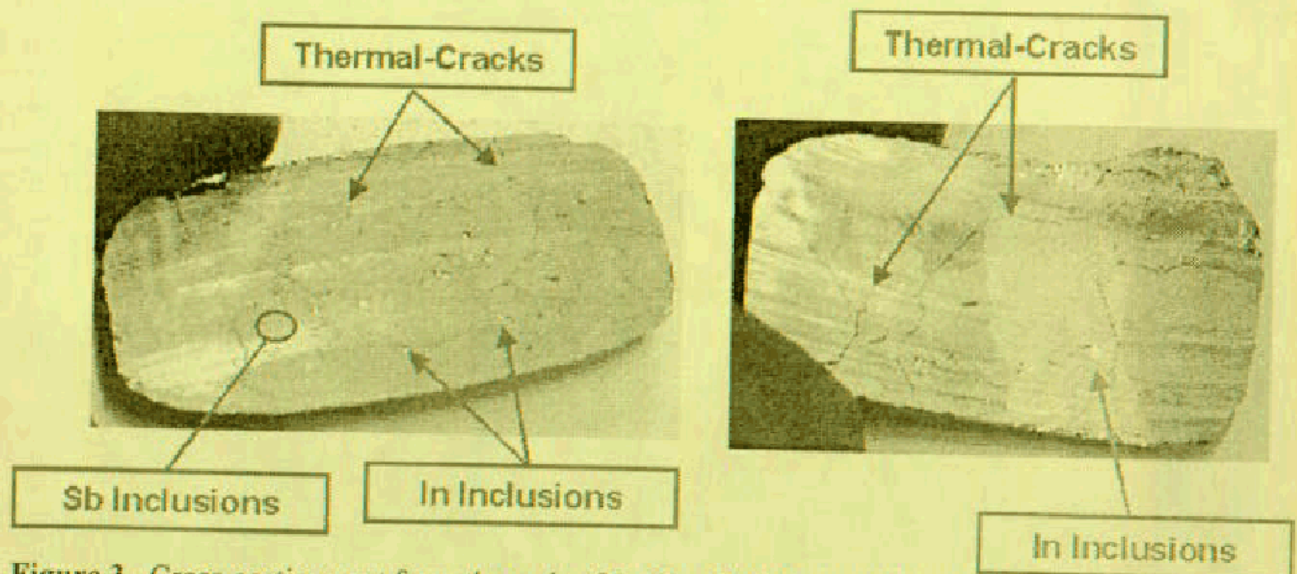

Figure 3. Cross-sections cut from the ends of $In_xGa_{1-x}Sb$ boules synthesized without rotation during solidification (left) and with ACRT during solidification (right). Indium and antimony inclusions along with thermal cracks are visible as noted. The "last-to-freeze" area of the crystal is towards the top of the figure.

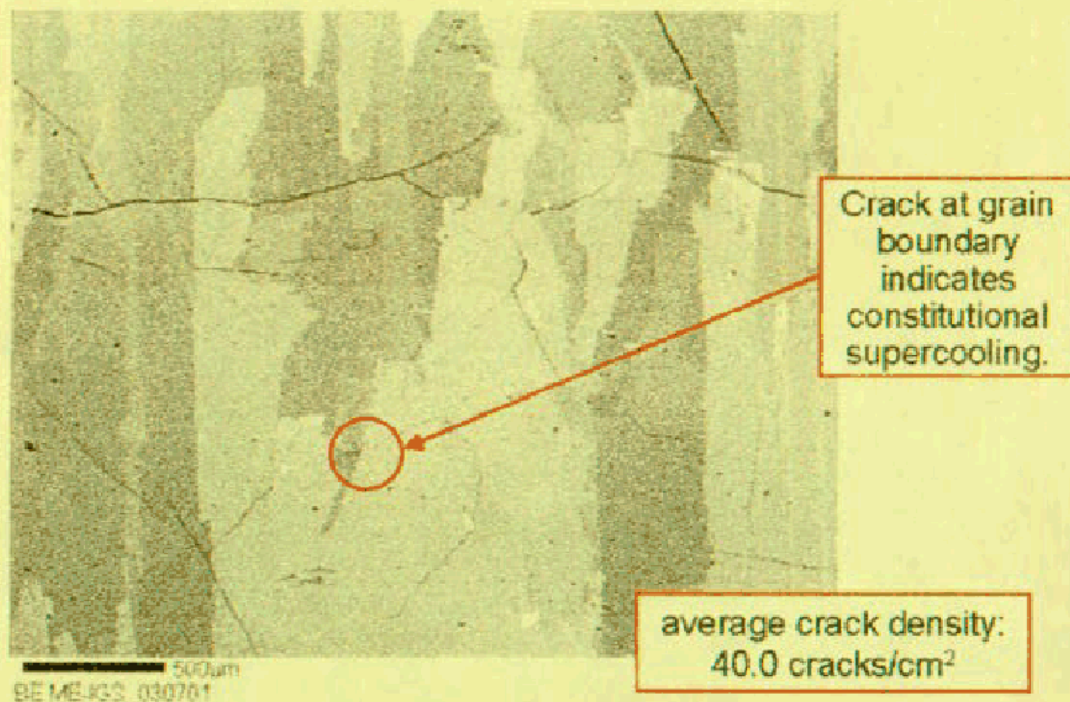

Figure 4. 500 micron SEM of a vertical cross-section of a boule synthesized without rotation during solidification. Composition is $In_{0.16}Ga_{0.84}Sb$.

A similar SEM image was taken of the sample synthesized with ACRT rotation during solidification. This image shows one large thermal crack and a few smaller micro-cracks. Enhancing this image to the inset shown, the thermal crack crossing the grain boundary is shown, with very fine micro-cracks that begin or end on the small visible grain. The rate calculated from 500 micron-scale scans of this sample evidence a micro-crack density of 1.7 cracks per square centimeter.

CONCLUSIONS

A comparison of two SEM images taken of ternary samples of $In_xGa_{1-x}Sb$ for x equal to 0.15 +/- 0.01 composition, has been made. A 95.8 percent reduction in micro-cracking has been observed using ACRT. Both experiments also utilized a high temperature gradient during growth, which enhances diffusion-controlled removal of solute products from the growth interface, but also contributes to thermal cracking of the material post-solidification.

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Ronald Gutmann and Prof. Krishna Rajan of Rensselaer Polytechnic Institute, Troy, New York, and Mr. Gregory Nichols of Lockheed Martin Corporation of Schenectady, New York, for valuable discussion during the course of this research.

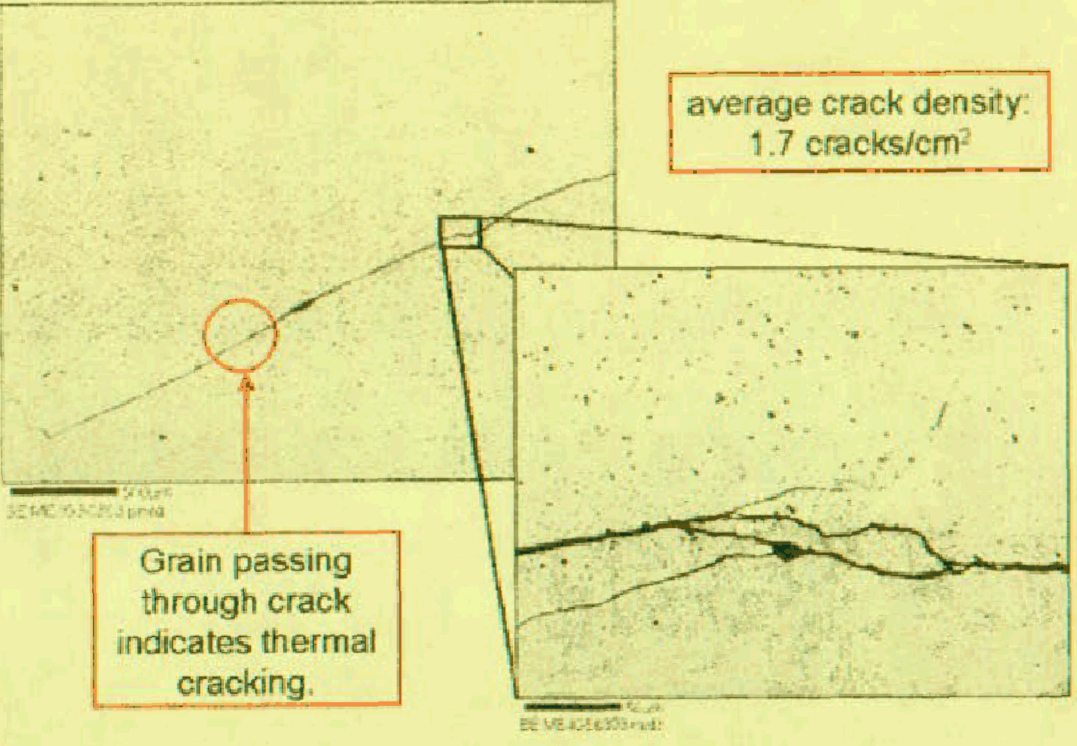

Figure 5. 500 & 50 micron SEMs of a vertical cross-section of a boule synthesized with ACRT during solidification. Composition is $In_{0.15}Ga_{0.85}Sb$.

REFERENCES

1. K.J. Bachman, F.A. Thiel, and H. Schreiber, Jr., Progress in Crystal Growth and Characterization **2**, 171 (1979).
2. P.S. Dutta and A.G. Ostrogorsky, Journal of Crystal Growth **198/199**, 384 (1999).
3. P.S. Dutta, A.G. Ostrogowsky, and R.J. Gutmann, in Thermophotovoltaic Generation of Electricity: Fourth NREL Conference, T.J. Coutts, J.P. Benner, and C.S. Allman, eds. (1999).
4. H.J. Scheel and E.O. Shultz-Dubois, Journal of Crystal Growth **8**, 304 (1971).
5. H.J. Scheel, Journal of Crystal Growth **13/14**, 560 (1972).
6. D. Elwell and H.J. Scheel, *Crystal Growth from High-Temperature Solutions*, (Academic Press, New York, 1975) p.392.
7. K. Nakajima, T. Kusunoki, and K. Otsubo, Journal of Crystal Growth **173**, 42 (1997)
8. P.S. Dutta & A.G. Ostrogorsky, Journal of Crystal Growth **191**, 904 (1998).
9. W.A. Tiller, *The Science of Crystallization: Macroscopic Phenomena and Defect Generation*, (Cambridge University Press, 1991)
10. R.T. Gray, Ph.D. Thesis, Clarkson University, 1991.
11. B.R. Pamplin, ed., *Crystal Growth, Volume 6 of International Series of Monographs in the Science of the Solid State*, (Pergamon Press, 1974.)