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Bulk growth of gallium antimonide crystals by Bridgman method

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Abstract. Gallium antimonide crystals were grown by the vertical Bridgman technique. Effects of ampoule diameter and dopant impurities (Te, P and In) on growth were studied. Crystal stoichiometry and homogeneity were verified with electron-probe microanalysis. Impurity distribution was investigated by secondary ion mass spectrometry (SIMS) and electron probe micro analysis. Variations of etch pit density (EPD) along the·length and the diameter were studied by image analysis method. Resistivity, mobility and carrier concentrations were measured along the length of the crystal.

Keywords. III–V semiconductor; gallium antimonide; crystal growth; Bridgman technique; isoelectronic doping.

1. Introduction

High quality gallium antimonide (GaSb) crystals have grown in technological importance in recent years for the fabrication of photo-detectors, in the wavelength range 1·3–1·7 μm (Nagao *et al* 1981), and heterostructure detectors and lasers for fibre optic communications (Capasso *et al* 1980; Chiu *et al* 1986). GaSb has also got prime attention for quantum-well and superlattice structures (Munekata *et al* 1986; Santos *et al* 1988). For such devices good quality GaSb substrates are required.

The most widely used method to grow substrate quality material is the Czochralski (CZ) technique, but the crystals grown by this technique frequently show microfaceted growth and twins (Kumagawa 1978; Miyajawa *et al* 1980). Striations and heterogeneity of impurities, along the growth direction and transverse to it, are also observed in CZ-grown crystals (Chin and Bonner 1982; Sunder *et al* 1986). The travelling heater method is less studied for growing GaSb crystal because of extremely slow growth rate (Benz and Muller 1979). Recently single crystal GaSb has been grown by employing the horizontal Bridgman growth technique (Lewadowsky *et al* 1985). Crystals grown by vertical Bridgman technique generally showed polycrystalline nature (Harsy *et al* 1981; Lendvay *et al* 1985). However, Lendvay *et al* (1985) could grow bicrystals in space using the same growth technique. They observed the average etch pit density to be $6{\cdot}5 \times 10^5\ \mathrm{cm}^{-2}$ and $5 \times 10^5\ \mathrm{cm}^{-2}$ for terrestrial- and space-grown samples. Relatively less effort has been made to study crystal stoichiometry, impurity distribution, etch pit density distributions etc. on Bridgman-grown GaSb. The present investigation thus reports bulk growth of GaSb by the vertical Bridgman technique and effects of ampoule diameters and different dopant impurities on the quality of the crystal. The crystal stoichiometry was verified by microprobe analysis at different positions of the ingot to study the crystal homogeneity. The impurity and etch pit density distributions were studied by secondary ion mass spectrometry (SIMS), electron probe micro analysis (EPMA) and image analysis, respectively. Variations of electrical properties along the length and the diameter of the crystal were investigated for the first time for Bridgman-grown GaSb.

2. Growth

All the crystals were grown from stoichiometric melt with slight excess of antimony to compensate for its loss during synthesis and growth. The synthesis was done from 5N or 6N purity Ga and Sb either in an argon atmosphere or in a vacuum of 10^{-6} torr. The growth procedure has already been reported (Basu and Roy 1986; Roy and Basu 1987), but is described briefly below. The growth was carried out in a conical-tipped quartz ampoule, in which the required amounts of Ga and Sb were placed and sealed at a vacuum of 5×10^{-6} torr. Synthesis was carried out either in an argon atmosphere at 900°C for one and a half hours or in vacuum in a sealed quartz ampoule at 800°C for two hours. The temperature of the furnace was raised at a rate of 250°C/h. After the synthesis, the ampoule was kept in the Bridgman furnace as shown in figure 1 and heated to 740°C for 2 h. The ampoule was then lowered with the help of a slow speed motor at the rate of 0·94 mm/h upto 510°C and 9·4 mm/h upto 300°C. Finally the furnace was cooled to room temperature at a faster rate and the ingot was removed from the ampoule.

3. Characterization

Formation of GaSb crystals was confirmed by the X-ray powder diffraction method. The surface morphology of the crystals were studied with a high resolution

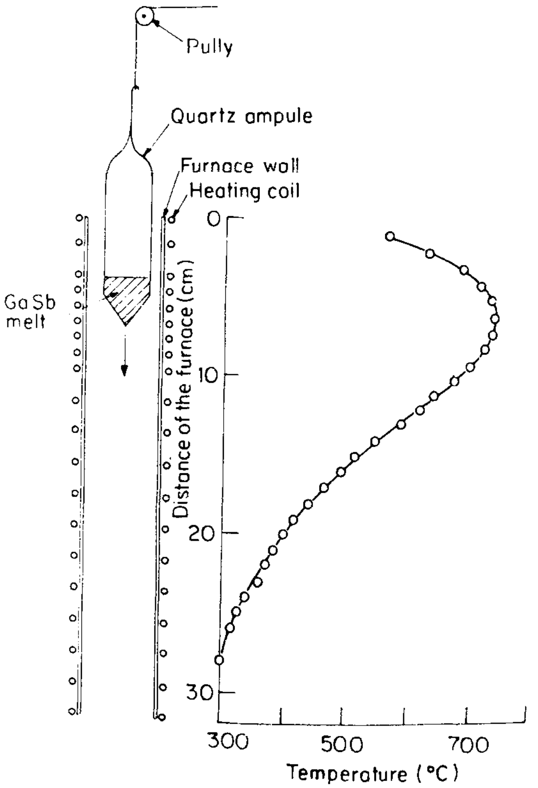

Figure 1. Schematic of vertical Bridgman growth unit along with the temperature profile of the resistance-heated furnace.

optical microscope. The variation of etch pit density (EPD) was investigated by image analysis method using a Texture Analysis System (Leitz, Germany). The Ga to Sb ratio was determined by electron probe microanalysis. Impurity distributions, as already mentioned, were studied by SIMS and EPMA. The type of conductivity was determined by the hot probe technique and the electrical parameters were measured employing the Van der Pauw method, using indium for ohmic contact.

4. Results and discussion

Different ampoule diameters used were 1·5, 1·3, 1·1 and 0·8 cm. Effect of dopant impurities were studied using different doping elements like P, In (isoelectronic) and Te. The typical ingot is shown in figure 2, grown from an ampoule diameter of 0·8 cm.

The results are given in table 1. While the undoped GaSb grown from a 1·1 cm diameter ampoule was a single crystal, increasing or decreasing the diameter resulted in polycrystallinity. A similar effect was also observed by Harsy *et al* (1981) and it was suggested that for larger ampoule diameters, non-uniform heat conduction results in polycrystallinity, and for small diameters the *wall effect* is responsible for polycrystallinity. Incorporation of impurities during growth reduces the grain size of the ingots, as observed from table 1, which is mainly due to the strain developed because of the difference in the atomic sizes of the dopant species and the host atoms.

The surface morphology showed the presence of twins in almost all the crystals. The single crystal, however, showed a twin only near the (conical) tip. Figures 3 and 4 show typical twin structure and etch pit pattern, respectively. The EPD values were found to be higher near the core of the crystal as reported earlier (Roy and Basu 1988), and were attributed to the thermal stresses due to the radial temperature gradient. The EPD values were also observed to increase from the tip to the upper end.

The microprobe analysis showed fairly good stoichiometry and homogeneity of the crystal. Ga to Sb ratios varied between 0·99 and 1·02 from the tip to the upper end. At the upper end slight antimony loss due to volatilisation during growth was observed. The impurity profiles for Te (for Te-doped crystals), Si and O were

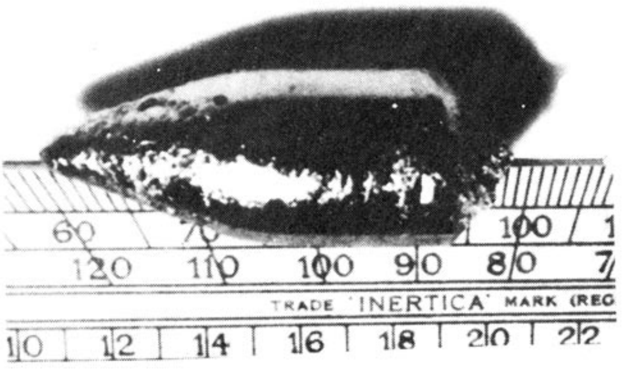

Figure 2. Typical GaSb ingot grown by the Bridgman method.

Table 1. Electrical properties of GaSb crystals grown under different conditions.

Sample*	Ampoule diameter (cm)	Doping element	Nature of ingot	Type of conductivity	Resistivity (ohm. cm)	Hall mobility ($cm^2/V\cdot s$)	Carrier concentration ($cm^{-3} \times 10^{17}$)	Average grain size (cm)	Average EPD ($cm^{-2} \times 10^5$)
1	1·5	Undoped	Polycrystal	*P*	0·056–0·058	422–521	2·64–2·07	0·51	2·7
2	1·3	Undoped	Polycrystal	*P*	0·046–0·054	232–368	5·83–3·15	0·66	—
3	1·1	Undoped	Single crystal	*P*	0·051–0·064	440–417	2·78–2·36	—	1·6
4	0·8	Te-doped ($4{\cdot}4 \times 10^{16}$ cm^{-3})	Polycrystal	*P*	0·083–0·095	394–527	1·91–1·25	0·21	1·5
5	1·1	Te-doped ($3{\cdot}5 \times 10^{18}$ cm^{-3})	Polycrystal	*n*	$2{\cdot}8$–$4{\cdot}3 \times 10^{-3}$	1870–2217	11·9–6·55	0·56	1·8
6	1·1	P-doped (8×10^{18} cm^{-3})	Polycrystal	*P*	0·054–0·061	214–422	5·44–2·42	0·1	4·5
7	1·1	In-doped ($2{\cdot}1 \times 10^{18}$ cm^{-3})	Polycrystal	*P*	0·063–0·062	498–445	1·99–2·26	—	2·7

*Samples 1 and 7 were grown from 6N purity starting materials; Other samples were grown from 5N purity materials.

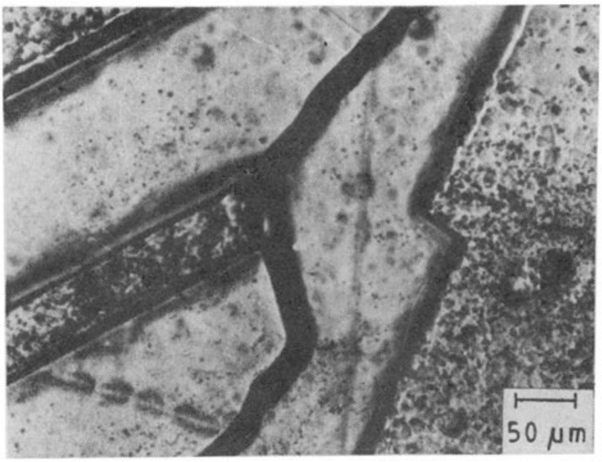

Figure 3. Optical micrograph of grain boundary and twin. Etchant $- 1HNO_3 + 1HF + 1H_2O$ for 15 s.

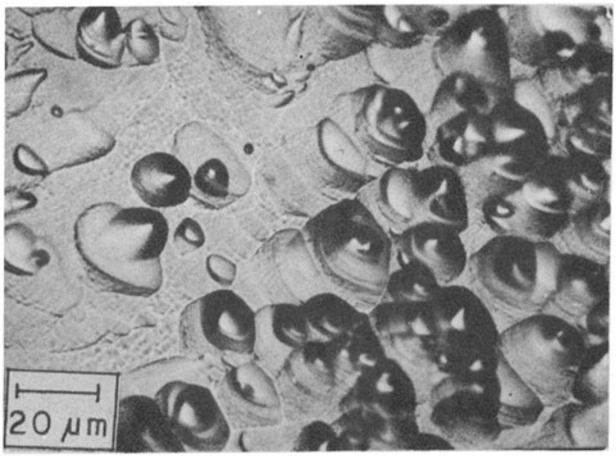

Figure 4. Optical micrograph of etch pits. Etchant $- 1HNO_3 + 1HF + 1H_2O$ for 15 s.

recorded by SIMS depth profiling and EPMA, along the length of the crystal, and transverse to it. No fluctuation of Si and O was observed from the SIMS profile upto 0·15 μm, but a little fluctuation of Te ($\approx$0·02%) was observed along the length of the crystal as shown in figure 5.

The values of the electrical parameters e.g. resistivity, mobility and carrier concentrations are given in table 1. The carrier concentrations were found to increase from the tip to the upper end which might be due to the segregation of impurities near the upper end of the ingot during the lowering of the ampoule from the Bridgman furnace. The highest electron and hole mobilities were found to be 2217 $cm^2/V{\cdot}s$ and 520 $cm^2/V{\cdot}s$ corresponding to the electron and hole concentrations of $6{\cdot}55 \times 10^{17}$ cm^{-3} and $2{\cdot}07 \times 10^{17}$ cm^{-3}, respectively. The lowest average EPD value ($1{\cdot}6 \times 10^5$ cm^{-2}) so far reported was observed for an undoped single crystal.

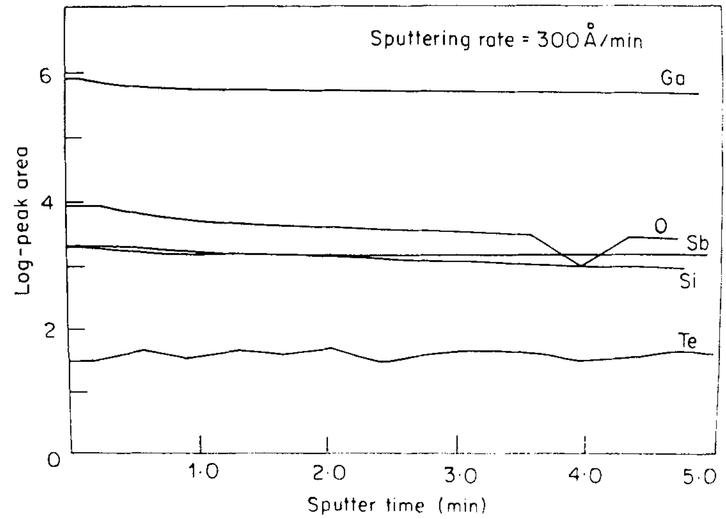

Figure 5. SIMS depth profile of Ga, Sb and impurities (Te, O and Si).

5. Conclusion

Good quality GaSb single crystals could be grown by the vertical Bridgman method. The EPD value, $1{\cdot}6 \times 10^5$ cm^{-2}, was found to be the lowest so far reported for Bridgman-grown GaSb crystals.

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