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## On the conduction mechanism of p-type GaSb bulk crystal

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# 1. Introduction

Among the III–V semiconductors, gallium antimonide (GaSb) is an interesting material due to their applications as substrate for the development of optoelectronic devices with a band-gap emission in the range from 1.1 to 3.9 mm being useful for applications in optical fiber communication systems [1].

From the device point of view, gallium antimonide (GaSb) based structures have shown potentiality for applications in laser diodes with low threshold, photodetectors, super lattices with tailored optical and transport characteristics. Consequently, GaSb based binary and ternary alloys have turned out to be important candidates for applications in longer wavelength lasers, photodetectors for fiber optic communication and high speed duple heterojunction bipolar transistor. These have stimulated a lot of interest in GaSb for basic research as well as device fabrication [2–7].

Although GaSb crystals are widely grown by Czochralski method [8], the Bridgman method is currently widely used to produce good quality GaSb crystals [1,9–12].

Nominally, undoped GaSb is p-type due to native acceptor background impurities which can be identified at low-temperature PL spectra through transitions involving bands, and donor–acceptor pairs. These native acceptors are related to Sb deficiency ( $V_{Sb}$ ), Ga vacancies ( $V_{Ga}$ ), gain Sb sites with double ionizable nature and Ga<sub>Sb</sub>V<sub>Ga</sub> complexes. These impurities are widely held identified as native acceptors, irrespective of the growth technique and growth conditions [13,14].

## ABSTRACT

Bulk crystals of gallium antimonide were grown using the vertical Bridgman techniques. The phase formation was confirmed by XRD studies. From dc and ac conductivity measurements, the conduction mechanism was investigated. The mobility ratio and the effective mass ratio were calculated to be 1.56 and 3.36 respectively. The measurements reveal higher values of power factor than the published results for the same compound.

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In this paper, I present the results of the experiments carried out to obtain low-defect GaSb crystals by the modified vertical Bridgman method. Results of the characterization studies such as XRD, EDX, electrical and thermoelectric properties of the grown crystals are also discussed.

#### 2. Experimental

#### 2.1. Crystal growth

For preparing homogenized GaSb crystals, since the atomic weights of Ga and Sb are 69.72 and 121.75 amu respectively, the ratio by weight should be 1:1.75. High purity 99.9999% Ga, and Sb (they were obtained from Aldrich) were used as starting material. Extreme care was taken in the transfer of material to maintain the accuracy to the level of  $\mu g/g$  of material. The materials were weighed by high sensitive rate and then transferred carefully to the ampoule, which previously was weighted empty, and then reweighing the ampoule after the development of materials to make sure the weight of the starting material.

The modified vertical Bridgman technique was used to grow pure GaSb crystals. As crucibles, high quality quartz ampoules (with a proper conical tip at the bottom to facilitate nucleation for crystal growth) sealed at  $10^{-4}$  Pa were used. The sealed ampoule was loaded into the sample holder and the furnace temperature was increased to 800 °C and the melt was homogenized for 12 h. The growth was carried out at a rate of 3 mm h<sup>-1</sup> in a modified [traveling solvent method (TSM)] Bridgman technique having a temperature gradient near 12 °C/cm. More details about this technique can be found elsewhere [15].

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## 2.2. Characterization

The surface of the grown crystals was analyzed by scanning electron microscopy. Also the homogeneity of the grown crystals was investigated with the aid of melting point test and electrical conductivity measurements of many cuts of each crystal.

The EDX analysis was performed by (Elemental Analyzer EDXRF, JSX3222, JEOL, Japan). The X-ray diffractograms were measured stepwise with angle/s value of 0.02° at ambient temperature with a model D 5000 Siemens diffractometer (Germany).

For the dc electrical conductivity measurements, the sample dimension was adjusted to be  $9 \text{ mm} \times 3 \text{ mm} \times 2 \text{ mm}$  by gentle cleavage and with the aid of fine polishing papers (0.5 Leco mark, USA). I used liquid nitrogen to cool the sample under room temperature. For the ac electrical conductivity measurements, the original shape of the product crystal was utilized, that is, the cylindrical form. Only the length was adjusted by polishing processes to be 4 mm while the crystal natural diameter was 10 mm. A two-part calorimeter was used. The inner part acted as a holder where the crystal was mounted on a flat end of a copper cylinder. It was heated electrically (the flat end was insulated from the crystal by thin sheets of mica). The second part of the calorimeter acted as a jacket to keep the measurements under vacuum.

For thermoelectric measurements, the values of the thermoelectric power  $\alpha$  were obtained by measuring small potential differences along the length of samples during slow and gradual increase and decrease of a small temperature gradient (the largest temperature difference between both ends of sample being about 5 K). The temperature difference ( $\Delta T$ ) was controlled in a differential mode with temperature controller (type elcont and eliwell). A very sensitive potentiometer (UJ33-E Mark) was used to measure the potential difference between both ends.

The silver conducting paste contacts were soldered on the GaSb to carry out the electrical conductivity and thermoelectric measurements. We put a small point of silver paste on each contact area of a polished GaSb. The contacts were let to dry off in air and after that the specimen was annealed in evacuated atmosphere at 100 °C.

The ohmic nature of the contacts was verified by recording the current–voltage characteristics for forward and reverse directions. From the current–voltage characteristics, the ohmicity coefficient has the nearest value to 1. So the silver conducting paste was successfully employed as a contact.

In this work, three different cuts from the virgin ingot (near the region corresponding to the beginning of the solidification process, the centre and the region corresponding to the final stages of the growth process) were prepared for both electrical and thermoelectric power measurements. No main differences were detected in the results and the general behavior.

## 3. Results and discussion

## 3.1. Structural characterization

The EDX analysis was made at five different places of the sample and it was found that the composition was uniform throughout the sample. From the corresponding EDX spectrum of GaSb, the Ga/Sb ratio (at.%) was found to be 0.99 (Fig. 1).

The X-ray diffraction (XRD) pattern obtained at room temperature for the grown GaSb sample is shown in Fig. 2. Indexing and refinement of XRD pattern indicate the presence of a single-phase crystalline structure for the synthesized materials. The X-ray pattern confirms the existence of face centered cubic (FCC) structure with the reflection arising from 111, 200, 220, 311, 400, 331 and 422 planes. The grown sample has good crystallinity and can be



Fig. 1. EDX spectrum of GaSb.

indexed with the Joint Committee on Powder Diffraction Standards (JCPDS) file 7–215 [16].

The lattice parameter for the obtained crystals is 6.092 Å, where the lattice parameter for the standard GaSb is 6.095 Å [16]. This result verifies the identity between the grown crystals and the standard one.

Crystallite size (D) of the obtained GaSb crystals was calculated to be 69.8 nm from the Debye Scherrer's formula [17].

#### 3.2. Dc conductivity studies

The dc conductivity measured in the temperature range 253–420 K exhibits semiconducting behavior, with conductivity growing from  $5.9 \times 10^{-3}$  to  $8.69 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$  at room temperature (Fig. 3).



Fig. 2. XRD spectra of GaSb crystals.

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