DEVELOPMENT OF DIRECTIONAL SOLIDIFICATION SYSTEM AND SYNTHESIS OF GALLIUM ANTIMONIDE AND ITS CHARACTERISATION

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Abstract

The rapid advancements in optical communication technology led intensive research and developmental study on the specific opto-electronic materials such as gallium antimonoide (GaSb) and indium antimonoide (InSb). In view of their potential applications in select data storage, conversion and mixing of frequency and parametric oscillations etc. have instigated a lot of interest for research and fabrication of GaSb devices. Purity of these compounds plays a major role in realizing the superior material properties and thus these high purity materials used in the fabrication of quality devices for high end applications. The system and the process helps in reduction of vibrations during the synthesis and crystallization process and thus yields GaSb compound in high pure form. This paper presents the design and development of directional freezing, solidification system and preparation. The characterization analysis by XRD, SEM and TEM techniques for high pure gallium antimonoide (GaSb) compound.

Keywords: *Gallium Antimonoide, Characterization, Directional Freezing and Solidification*

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I. INTRODUCTION

GaSb is one of the important primary materials used in the fabrication of various electronic devices such as LEDs, infrared detectors, lasers, transistors and photovoltaic cells etc. [1-3]. GaSb based devices works in the band gap range of 0.17 eV at 300K (infrared wave length 6.2µm) and useful to infrared (IR) related optoelectronic applications using GaSb. GaSb also possess some special properties such as low electron mass, high mobility, lattice match with select ternary and quaternary III-V semiconductor materials [4-5] and thus making it a most suitable substrate material. Bridgmann and Czochralski methods[6] are employed to grow quality GaSb bulk crystals. Bulk crystals grown by employing Bridgmann technique contain structural defects. GaSb compound is synthesized by mixing with the appropriate amounts of input and starting materials of gallium and antimony. 7N purity level of (99.99999) implies that, the levels of impurities present in the synthesized GaSb compound is less than 100 ppb and major metallic impurities in starting materials includes Cd, Fe, Si, Ge, Cu, Zn and Al. The presence of gaseous impurities such as carbon and oxygen should be controlled and less than to 1 to 10 ppb range. Presence of impurities in the starting materials and also in the synthesized GaSb compound will mainly contribute to deep and shallow energy levels within the energy gap and thus leads to performance failure of device. . Hence purity analysis and property study with stringent accuracy and consistency employing Inductively Coupled Plasma Mass Spectrometry (ICP-MS), GDMS(Glow Discharge Mass Spectrometry) etc. techniques become more important.

II. DESIGN AND DEVELOPMENT OF PROCESSING SYSTEM

Ultra high purification of gallium, indium and their select alloys is fraught with the following material process related inherent problems and associated instrumentation difficulties. a) Design and development of zone-melting and crystallization temperature, operational conditions and to realize system, one has to revolve around process modeling and rely on the data base from the design and development of prototype test zigs and their performance tests and capability demonstration. b) creation and maintaining of narrow solid-liquid regions and interface of desired length and width, when multi heater-coolers were used and kept stationary, c) sample tube rotational speed and movement of direction were studied. d) heat transfer between heater and sample tube. The above problems leads to a non-uniform composition and resulting in making segregation more complex and reducing the reproducibility as well, the stagnation of a high concentration of impurities at the interface stages, affecting the efficiency of refining. Vertical

gradient freeze (VGF) technique is mostly employed in the preparation and growth of quality crystals as controlled and vibration less beneficial growth features helps and plays a major role in controlling the defects [2].Several researchers have reported growth and characterization aspects of GaSb [3-4]. The design and development of *directional freezing and solidification system(DFSS)* for synthesis and purification of GaSb compound consists of development and integration of sub systems such as a) furnace, b) programmable logical controller based control system, c) translation assembly d) rotational assembly. Figure 1 illustrates the DFSS system

Fig. 1. Directional freezing and solidification system(DFSS)

The following considerations were taken into account in the design and development of furnace: a) distribution of desired temperature within furnace. b) the temperature at the top of the furnace should be high and this temperature should be gradually decreases while going down to reach the lower part of the furnace. The furnace is thermally controlled such that its heat input is configured in such a way that the melting point of the material is more or less the midpoint of the sharp temperature drop. The temperature drop at the bottom could be more rapid compared to top of the furnace. However, such a rapid drop should not be so large because it could make havoc in cooling of samples. In most of the cases the temperature at the bottom is maintained at room temperature. The furnace comprises super kanthal based heating elements wounded on quality ceramic tube of 2 mm wall thickness, 50 mm diameter and 500 mm length and covered with ceramic powder coating, thermal insulation and the furnace will provide maximum heating temperature up to 1000 C. The PLC based controlled system is used to control the temperature of furnace, translation and rotation of sample containing ampoule in the *DFSS* system. The other sub systems include thyristor based controllers to control power voltage, temperature transmitter to measure and amplify output signal, programmable logic controller for conversion of analog to digital or digital to analog and a stepper motor with driver unit to position the ampoule at desired zone. The complete setup is controlled using lab view software package which is interfaced through PLC.

III. EXPERIMENTATION

The intent of experimentation is to segregate select impurities like Li, Na, Cr, Fe, Ni, Sr, Cd, Sn and Hg during the purification and crystallization processes of GaSb. Experimental methodology include homogenization, synthesis and directional freezing and solidification on 4N +/ 5N pure GaSb. Four batches of purification and crystallization experiments on GaSb, each-25 gram level were carried out. For homogenization, treated Ga and Sb metals were loaded into the quartz ampoule and sealed under vacuum of 5 x 10^{-6} Torr level. The sample was then heated at 750^0 C for melting, further was subjected for freezing at 10^0 C and again was heated to re-melt at 750^0 C with 12 hrs pass (es) and 3 cycle (s) scheme. Samples that were formed by homogenization were taken out from the ampoule in a clean room (1000 class/100 class) environment and are finely crushed into powder. These powder samples were once again loaded into the quartz ampoule and were sealed under the vacuum of $5x10^{-6}$ Torr level. Samples in the ampoule were further subjected to vertical directional freezing and solidification (710-720 ^{0}C). This solidification process was performed with 24 hrs pass time, travel rate of 25-35 cm.hr^{-1}, rotation rate of 35-45 rpm and 3 cycles-pass (es) scheme. The prepared purified sample was cut into three portions and the samples were evaluated employing XRD, SEM, TEM and Raman spectrum methods. During pre and final purification processes, clean environment (10000/1000 class) and clear laminar flow benches (100 class) were used. GaSb is relatively less toxic but still, adequate safety precautions were followed and glove box facitlities were used. While handling chemicals and pure GaSb. the cleaning procedures that were followed include treatment of starting materials, prepared GaSb compund, crucibles with electronic grade trichloro ethylene, washing through pickling with acetone, methanol and nano-pure water, preparation of ultra pure aqua regia i.e 1:1 ratio $HCl+HNO_3$, treatment of beakers and crucibles with electronic grade aqua regia for 2 hours, cleaning crucibles with super pure aqua regia for removing oxide layer. Figure 2 shows homogenised and crushed GaSb powder and Fig.3 shows the synthesised and purified GaSb

Fig.2. Homogenised and crushed GaSb Power

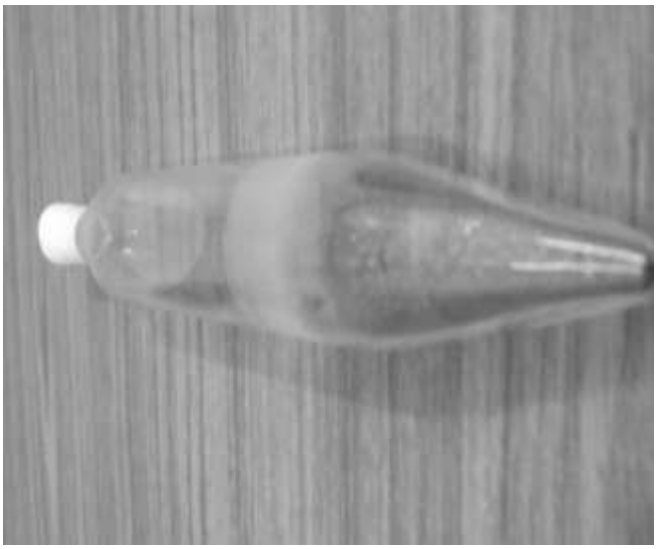


Fig.3. Synthesised and purified GaSb Purified GaSb

IV. RESULT AND DISCUSSION

In Fig. 4, the XRD patterns of GaSb are presented and XRD patterns are recorded in the range of 2 theta (4–80 ˚ using CuK radiation. The XRD spectra revealed that the GaSb are poly-crystalline structure. The thin films are dominated by three principal orientations: (111), (220) and (311). Typical XRD experimental measurement results of the (GaSb-03) are given here: lattice spacing d =2.15607^{O}A, 2θ = 41.865. The crystallographic direction is determined and shows the single peak at 2θwith (220) direction. These data are compared with the diffraction data: ASTM, JCPDS 7-215 of GaSb; where d = 2.156 ^{O}A, hkl (220), 2θ = 41.8639. The relative peak intensity is proportional to the crystalline material perfection, the higher the peak is, the higher the quality of crystal is. The large counts, sharp peaks reveal the reduction in defects level.

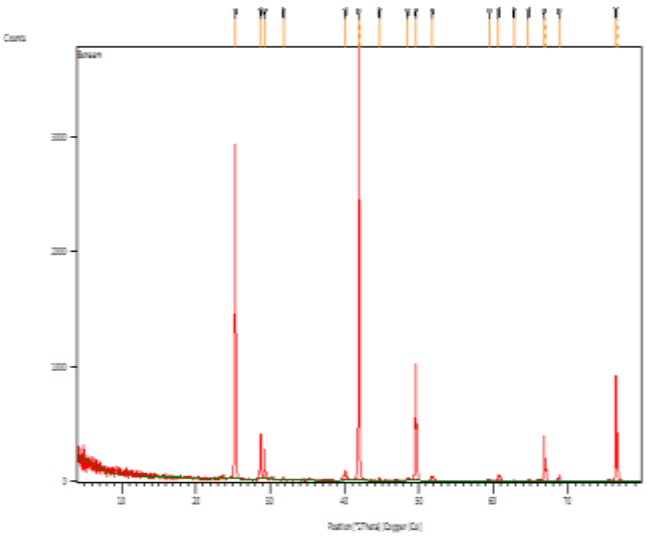
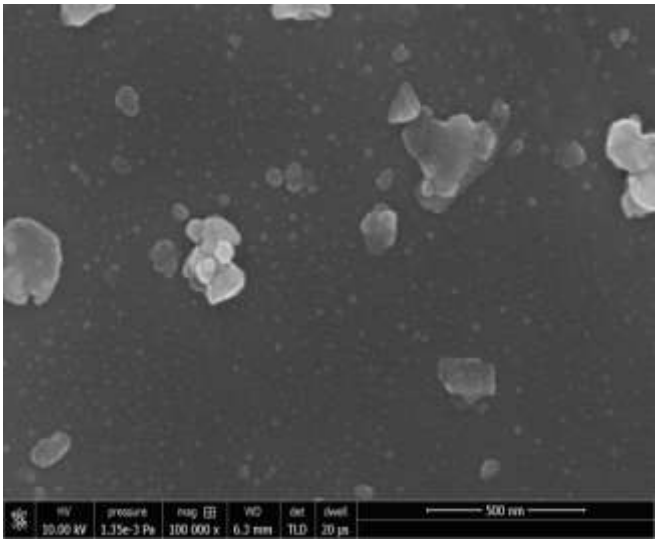
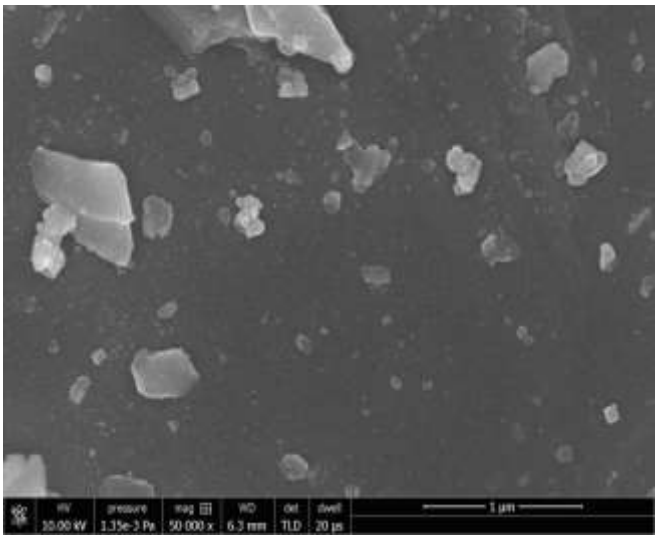


Fig. 4. XRD spectrum -GaSb

In **Fig.5**, different surface morphology and microstructure features were observed for different GaSb samples with micro regions of impurities inclusions and segregation and micro cracks. Also oxygen, carbon presence as surface contamination is seen. Grains become densely packed as shown in SEM surface morphology. The grain size varies and the average grain size is 1 µm, 4 µm, 5 µm, 10 µm, 50 µm and 400 µm. These microstructures were invariably observed at the centre of the ingot and length gradually decreased towards the direction of periphery In **Fig.6**, TEM enables the observation of dislocations and crystal defects inside the bulk sample. Sample preparation is a critical step in TEM characterization and GaSb samples must be thinned to transmit electrons (less than 100 nm) provided it keeps stable under incident of high energy electron in a vacuum environment. The TEM image is taken from the 500 Nm under bright field. The TEM results show that 500 µm GaSb, the dislocations originate from the interface and propagate with GaSb samples. **Fig.7,** SEM-EDAX results show that prepared GaSb samples contain oxygen and carbon inclusions and impurities. **Fig.8**, Raman spectrum shows that the highest transmission which confirms the single oriented of growth of sample. and improved crystal structure and quality. Raman scattering measurement is easy and sensitive to probe the defects.





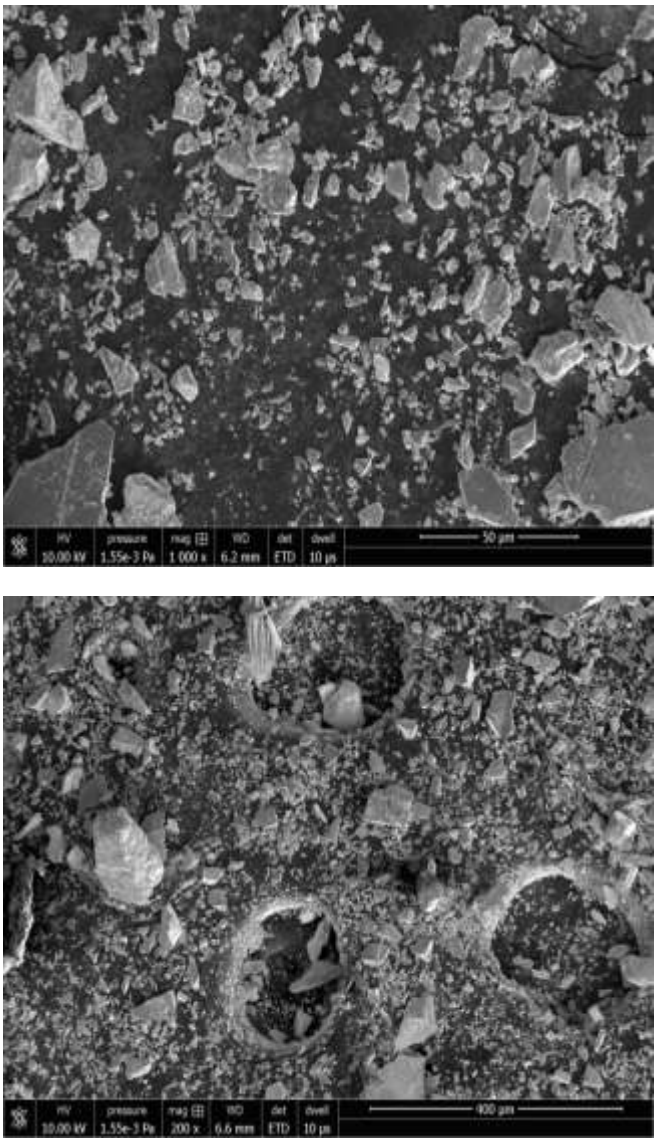
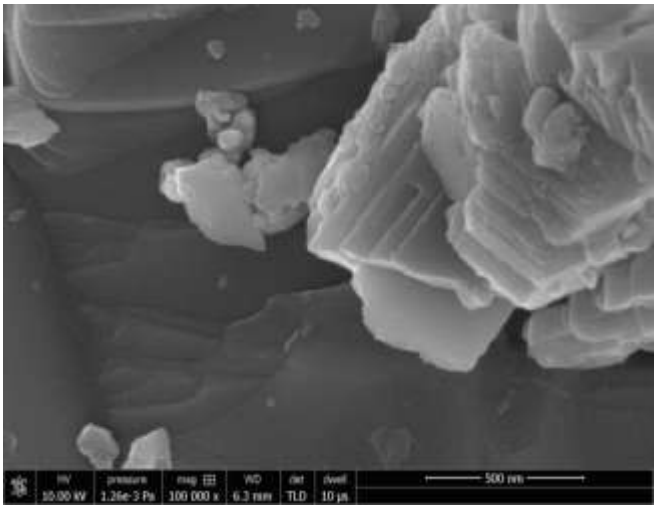


Fig. 5 SEM images of GaSb samples



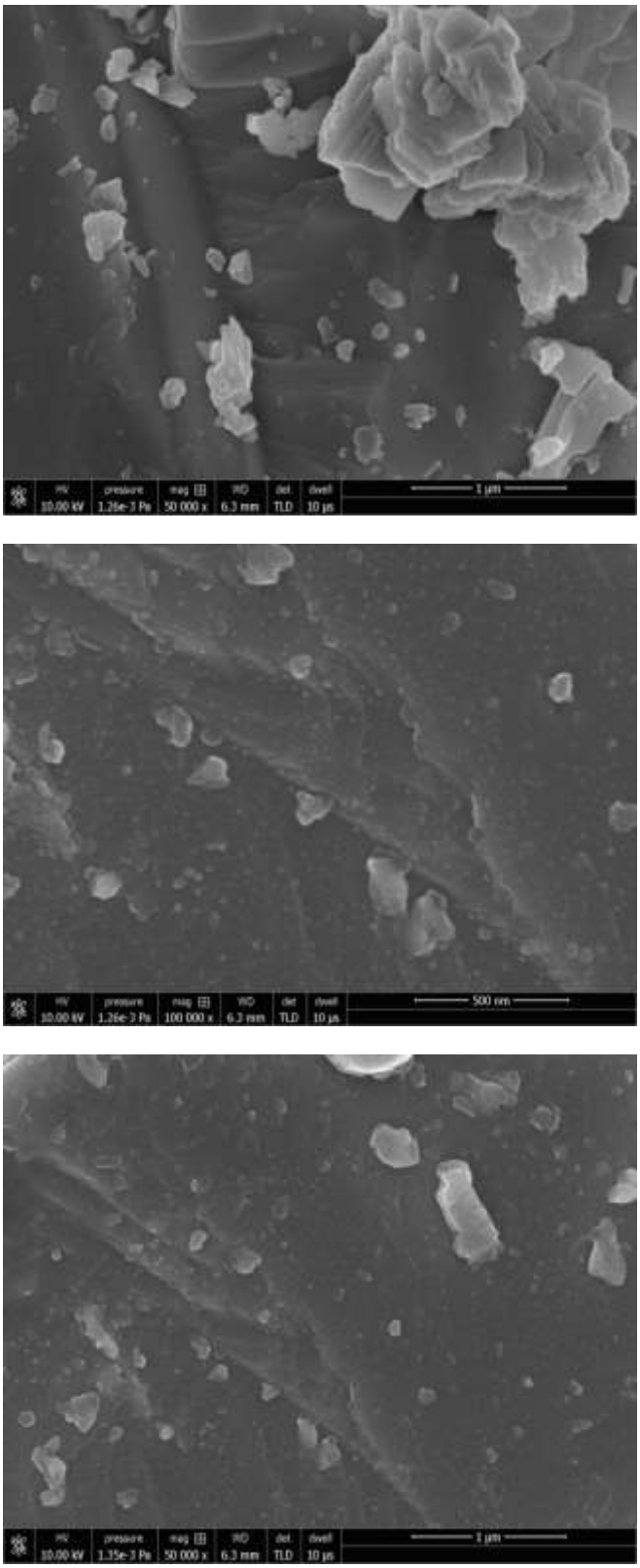


Fig. 6. TEM images of GaSb samples

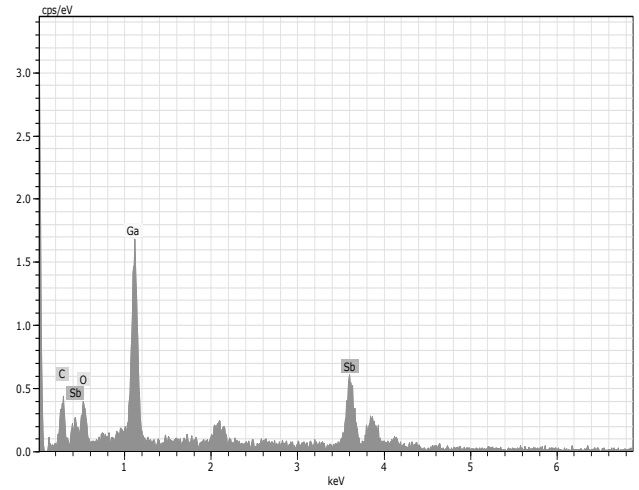


Fig.7. SEM-EDAX spectrum of GaSb sample

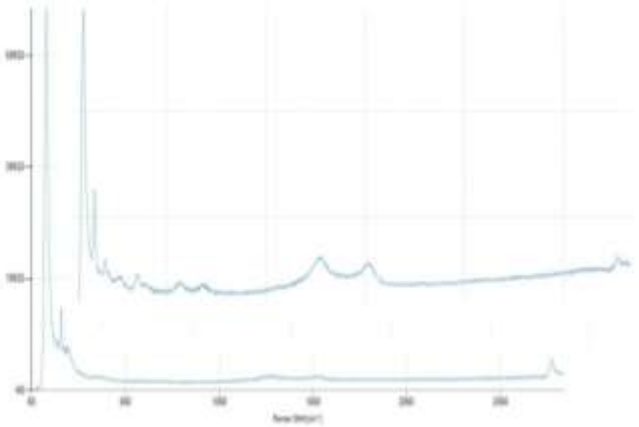


Fig. 8 Raman Spectra of GaSb

V. CONCLUSION

Directional solidification system for preparation of high pure gallium antimonoide (GaSb) compound was designed and developed. The performance and capability of the system were also been demonstrated through purifying and preparation of GaSb compound. Process parameters including a) temperature gradient and creation and maintaining of narrow solid-liquid regions, b) interface of desired length and width, c)The sample tube rotational speed movement of direction were studied. Prepared GaSb samples were characterized employing , XRD, SEM, TEM, and Raman Spectra Techniques.

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