As-grown, undoped III-antimonide bulk substrates contain high concentration of native defects resulting in high residual carrier density. In this paper, we have demonstrated that native defects can be compensated in bulk substrates of GaSb, InSb, and Ga$_{1-x}$In$_x$Sb via impurity doping and low temperature growth from nonstoichiometric melts and solutions. Decrease in residual carrier concentration up to one order of magnitude at 300 K and three orders of magnitude at 77 K have been achieved.

Keywords: GaSb; InSb; GaInSb; compensation; low temperature growth; native defects

1. Introduction

III-Antimonide compound semiconductors are of particular interest amongst III-V semiconductors since the band gap can be tuned from approximately 0.17 to 1.6 eV. Furthermore, the possibility for band gap engineering in the 6.1 to 6.5 Å lattice constant range offers extraordinary opportunities for the development of novel band aligned devices for high speed electronic and photonic applications operating between the 2 to 14 $\mu$m spectral region.\textsuperscript{1–6} Substrate properties play a significant role in the performance of devices. Antimonide based substrates are undermined by the high concentration of native defects (i.e. vacancies and antisites). For example, as grown undoped GaSb, InSb, and Ga$_{1-x}$In$_x$Sb exhibit high concentration of native defects and free carrier absorption.\textsuperscript{6–8} In this work, two methodologies have been employed to compensate native defects in vertical Bridgman grown bulk substrates of GaSb, InSb, and Ga$_{1-x}$In$_x$Sb.

GaSb substrates are readily available from commercial vendors. However, they are for the most part not optically transparent in the regions of interest and they are also highly conductive.\textsuperscript{9} These properties severely limit the performance of optical and electronic devices grown on GaSb substrates. As grown undoped GaSb is always p-type in nature irrespective of growth technique and conditions.\textsuperscript{7} Work over the last 3 decades has been devoted mainly for understanding the origin of the residual acceptors that are the limiting factors for both fundamental studies and device applications.\textsuperscript{7} The residual acceptors with concentration of $\sim 10^{17}$ cm$^{-3}$ have been found to be related to gallium vacancies ($V_{Ga}$) and gallium in antimony
site (GaSb) with doubly ionizable nature. Native defects in InSb have been studied by Kendall and Huggins; they studied the self-diffusion in InSb using radiotracers and refined sectioning techniques. They proposed the In:Sb divacancy as the defect primarily responsible for self-diffusion of both components in InSb. In addition, they reported that the diffusion coefficients of neither In nor Sb seemed to depend on the ambient Sb pressure. Kendall and Huggins showed that the native defect concentration in InSb can be greatly suppressed if the material is grown at low temperatures. However, to the best of our knowledge, no work has been reported in the low temperature bulk growth of InSb substrates.

The electrical properties of Ga$_{1-x}$In$_x$Sb have been investigated in detail by Joullie and co-workers. As-grown undoped Ga$_{1-x}$In$_x$Sb is n-type in nature above $x = 0.5$ and p-type for $x$ below 0.5. Therefore, it would be expected that at a composition $x = 0.5$, Ga$_{1-x}$In$_x$Sb would exhibit near intrinsic properties as the native p-type like defects from GaSb would compensate for the n-type like native defects inherited from InSb.

In this work, we have successfully achieved a high level of native defect compensation in GaSb, InSb, and Ga$_{1-x}$In$_x$Sb bulk substrates by implementing two specific approaches during the vertical Bridgman growth process. First, compensation of the residual native acceptor concentration in GaSb and Ga$_{1-x}$In$_x$Sb bulk crystals was achieved via tellurium doping of the melt during growth. Second, InSb bulk crystals were grown at temperatures below the eutectic melting point, ~525 °C, from indium rich melt compositions. The electrical and optical properties of the grown crystals are presented here.

2. Experimental Details

For the charge synthesis of bulk GaSb and InSb crystals, 7N pure Ga and 6N pure Te, In and Sb were used as-received without any chemical treatment. The typical melt height was between 2 and 4 cm. The temperature gradient imposed by the furnace near the melt-solid interface was approximately 5 °C/cm. Prior to the growth of GaSb, InSb, and Ga$_{1-x}$In$_x$Sb bulk crystals, the following growth procedure was employed. First, the starting source materials were elevated to a temperature 50 °C above the melting point of the binary material (712 °C for GaSb and 525 °C for InSb). Then, the melt was homogenized for 1 h by rotating the crucible at 120 rpm while a static stirrer remained in the melt within 0.5 cm from the bottom (where growth initiated) of the crucible. After homogenization, the crucible was lowered at a constant vertical translational rate of 1 cm/h (0.5 cm/h for Ga$_{1-x}$In$_x$Sb) and rotated continuously at 120 rpm, while the static stirrer remained in the melt within 0.5 cm of the solid-liquid interface at all times to keep the melt homogeneous. After the entire ingot reached outside the hot zone of the furnace, the crystal was cooled to room temperature over a period of 12 h by appropriately programming the furnace temperature-time profile.
For native defect compensation in bulk GaSb crystals, considering that undoped GaSb has between \((1 \text{ to } 2) \times 10^{17} \text{cm}^{-3}\) acceptors and the segregation coefficient of Te is 0.37,\(^1\) the initial Te concentration in the melt was set at \(1 \times 10^{18} \text{cm}^{-3}\) to obtain the highest level of compensation at approximately midway along the growth direction. Native defects in pure bulk GaSb crystals have segregation coefficient close to unity.\(^7\) Hence all the pure GaSb samples exhibited similar optical and electrical properties, substrate GS0. Several wafers were extracted from the region of highest compensation of the Te doped GaSb ingot, the mid region along the growth direction. The extracted wafers were labeled GS1 and GS2 respectively. Substrates GS1 and GS2 are located approximately 8 and 18 mm from bottom of the boule. Native defect reduction in InSb was achieved by the growth of the material from indium rich melts. As mentioned previously, Kendall and Huggins\(^1\) demonstrated that the concentration of native defects in InSb can be suppressed if the material is grown at low temperatures. Therefore, InSb crystals were grown from stoichiometric and indium rich melts. Thus, low temperature grown InSb crystals were obtained from temperatures varying from below the eutectic point, 525 °C, down to very close to the melting point of elemental indium, 150 °C, according to the InSb phase diagram.\(^1\) From the grown stoichiometric and nonstoichiometric InSb boules substrates IS1 and IS2 were obtained from approximately 4 and 18 mm from the bottom of the boules. Similarly, Ga\(_{1-x}\)In\(_x\)Sb bulk crystals were grown with an approximately \(1 \times 10^{18} \text{cm}^{-3}\) Te doping concentration and with a starting melt composition of \(x = 0.75\). Ga\(_{1-x}\)In\(_x\)Sb substrates with varying compositions \(x\) were obtained namely, substrates IGS1, IGS2, and IGS3. All substrates were polycrystalline, without inclusions, and their properties are tabulated in Table 1.

3. Results and Discussion

Table 1 displays the electronic properties of GaSb and InSb substrates for different growth conditions at 300 and 77 K. From the table it is observed that the properties for each substrate material vary depending on the growth conditions. If we look at the GaSb properties, we can observe that the carrier concentration of the undoped pure GaSb substrate (GS0) is almost an order of magnitude higher than that observed in the Te doped GaSb substrates (GS1 and GS2). The mobility of substrate GS0 is approximately 5 times larger than in substrate GS1 and 15 times larger than in substrate GS2. However, the resistivity observed in the Te compensated substrates are approximately 15 (GS1) and 300 (GS2) times larger than the resistivity observed for the undoped GaSb substrate (GS0). The effects of impurity compensation in GaSb have been observed and explained previously in the literature. Baxter et al.\(^1\) studied the behavior of the electron mobility in Te compensated GaSb samples at 77 K as well as in lithium diffused Te compensated GaSb samples at 300 and 77 K. They attributed the monotonic variation of mobility with carrier concentration to the dominance of impurity scattering under conditions of high compensation. Similarly, for InSb, in Table 1, it is observed that...
Table 1. Electrical properties of GaSb, InSb, and Ga$_{1-x}$In$_x$Sb bulk substrates at 300 and 77 K for various growth conditions.

<table>
<thead>
<tr>
<th>Material: dopant</th>
<th>Sample Name</th>
<th>Type</th>
<th>Temp. (K)</th>
<th>Carrier Conc. (cm$^{-3}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Resistivity (Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb</td>
<td>GS0</td>
<td>p</td>
<td>300</td>
<td>1.92×10$^{17}$</td>
<td>559.15</td>
<td>0.061</td>
</tr>
<tr>
<td>GaSb</td>
<td>GS0</td>
<td>p</td>
<td>77</td>
<td>2.38×10$^{16}$</td>
<td>1,973.90</td>
<td>0.13</td>
</tr>
<tr>
<td>GaSb:Te</td>
<td>GS1</td>
<td>p</td>
<td>300</td>
<td>2.66×10$^{16}$</td>
<td>129.35</td>
<td>1.83</td>
</tr>
<tr>
<td>GaSb:Te</td>
<td>GS1</td>
<td>p</td>
<td>77</td>
<td>3.50×10$^{13}$</td>
<td>48.15</td>
<td>3.720.00</td>
</tr>
<tr>
<td>GaSb:Te</td>
<td>GS2</td>
<td>n</td>
<td>300</td>
<td>1.16×10$^{16}$</td>
<td>39.65</td>
<td>16.40</td>
</tr>
<tr>
<td>GaSb:Te</td>
<td>GS2</td>
<td>n</td>
<td>77</td>
<td>1.16×10$^{14}$</td>
<td>38.40</td>
<td>323.96</td>
</tr>
<tr>
<td>InSb</td>
<td>IS1</td>
<td>n</td>
<td>300</td>
<td>2.59×10$^{17}$</td>
<td>4.79×10$^{4}$</td>
<td>3.12×10$^{-4}$</td>
</tr>
<tr>
<td>InSb</td>
<td>IS2</td>
<td>n</td>
<td>300</td>
<td>3.58×10$^{16}$</td>
<td>5.64×10$^{4}$</td>
<td>3.25×10$^{-3}$</td>
</tr>
<tr>
<td>Ga$<em>{0.68}$In$</em>{0.32}$Sb:Te</td>
<td>GIS1</td>
<td>n</td>
<td>300</td>
<td>2.93×10$^{17}$</td>
<td>7.03×10$^{3}$</td>
<td>3.41×10$^{-3}$</td>
</tr>
<tr>
<td>Ga$<em>{0.62}$In$</em>{0.38}$Sb:Te</td>
<td>GIS2</td>
<td>n</td>
<td>300</td>
<td>3.76×10$^{17}$</td>
<td>8.48×10$^{3}$</td>
<td>2.06×10$^{-3}$</td>
</tr>
<tr>
<td>Ga$<em>{0.58}$In$</em>{0.42}$Sb:Te</td>
<td>GIS3</td>
<td>n</td>
<td>300</td>
<td>4.92×10$^{17}$</td>
<td>1.46×10$^{4}$</td>
<td>8.70×10$^{-4}$</td>
</tr>
</tbody>
</table>

Note: Growth condition and sample thickness

- $a$: Unintentionally doped pure GaSb, 730 µm thickness.
- $b$, $c$: Te doped GaSb, (b) 390 and (c) 410 µm thickness.
- $d$: Unintentionally doped pure stoichiometric grown InSb, 620 µm thickness.
- $e$: Low temperature grown (∼275 °C) InSb from indium rich melt, 600 µm thickness.
- $f$, $g$, $h$: Te doped Ga$_{1-x}$In$_x$Sb, (f) 620, (g) 600, and (h) 740 µm thickness.

the displayed electrical properties for the low temperature grown substrates (IS2) are better than those observed in the high temperature grown InSb substrates (IS1). For example, the low temperature substrate IS2 shows lower carrier concentration, higher mobility, and higher resistivity compared to the high temperature grown substrate IS1. These data correlate with the expected native defect concentration results obtained by Kendall and Huggins$^{11}$ where low native defect concentration is expected for low temperature grown InSb. For the Te doped Ga$_{1-x}$In$_x$Sb substrates (GIS1, GIS2, and GIS3), we can observe from Table 1 that the electrical properties for $x < 0.42$ are very similar to the properties displayed by the low temperature grown InSb substrates (IS2). On the other hand, the electrical properties of the Te doped Ga$_{1-x}$In$_x$Sb substrates (GIS1, GIS2, and GIS3) do not compare well with the properties displayed by the Te doped GaSb substrates (GS1 and GS2). As we can see from Table 1, the carrier concentration exhibited by the Te doped Ga$_{1-x}$In$_x$Sb substrates (GIS1, GIS2, and GIS3) are about one order of magnitude higher and the resistivities are about three orders of magnitude lower relative to the Te doped GaSb substrates (GS1 and GS2). However, the electron mobility exhibited by the Ga$_{1-x}$In$_x$Sb substrates (GIS1, GIS2, and GIS3) are between two to three orders of magnitude higher compared to the Te doped GaSb substrates (GS1 and GS2).
which would be advantageous for high speed electronic and photonic applications.

![Near- and mid-IR transmission measurements of pure and Te compensated GaSb and InSb substrates at 300 K, in atmospheric ambient. (a) Sample GS0 corresponds to pure GaSb sample and samples GS1 and GS2 correspond to Te compensated GaSb samples. (b) Sample IS1 corresponds to pure InSb grown at the eutectic point, $\sim 525 \, ^\circ\text{C}$, and sample IS2 corresponds to low temperature grown InSb from an indium rich nonstoichiometric melt.](image)

Figure 1 displays the near- and mid-IR optical transmission properties of all GaSb and InSb substrates. From Fig. 1a, it is observed that the transmission properties exhibited by the Te compensated GaSb substrates, GS1 and GS2, are far more transparent and broad compared to the properties observed for the undoped GaSb substrates (GS0). Also, Fig. 1b shows that the transmission properties of the low temperature grown InSb substrates (IS2) are more transparent and broad compared to the transmission properties observed for the high temperature grown InSb substrates (IS1). Also, note the difference in the observed band edge between IS1 and IS2 which can be predicted by the Burstein-Moss shift. This further proves that indeed we have suppressed the free carrier density in InSb via low temperature growth. In fact, Fig. 1 helps to corroborate the electrical properties shown in Table 1. Table 1 and Fig 1 show a substantial decrease in carrier concentration, free carrier absorption, and an increase in resistivity for the Te compensated GaSb (GS1 and GS2) and low temperature grown InSb substrates (IS2) compared to the undoped GaSb (GS0) and InSb (IS1) substrates.

4. Conclusions

Suppression of native defects has been achieved in Bridgman grown bulk substrates of GaSb, InSb and Ga$_{1-x}$In$_x$Sb via impurity doping and low temperature growth.
Superior optoelectronic properties have been observed in the obtained substrates namely lower residual carrier concentration and free carrier absorption as well as higher resistivity compared to the undoped stoichiometric grown substrates.

Acknowledgments

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References