Improvements in Electrical and Optical properties of low bandgap III-V Antimonides by using Isoelectronic Dopants

A Chandola, Youngok Ko and P S Dutta*
Rensselaer Polytechnic Institute, Troy, NY.

Andrew Zakel, Leonel Gonzalez, Arlynn Hall, Jean Henry, G D Gillen and Shekhar Guha
Air Force Research Laboratory, WPFAB, OH.

Abstract. Vertical Bridgman grown bulk crystals of antimonides (e.g. InSb, GaSb & InGaSb) doped with isoelectronic dopants exhibited significant reduction in free-carrier absorption. The enhancement in below band gap optical transmission and reduction in residual doping concentration are attributed to reduction or compensation of native defects.

1. Introduction
Low bandgap III-V compounds are fundamentally interesting due to their low electron effective mass and high mobility. Due to their low bandgap, they can be efficiently used as IR detectors, emitters and photovoltaic energy converters. They also play an important role in high speed electronic devices. Many authors have investigated the optical properties of low bandgap III-V antimonides such as InSb [1-4 and references therein] and GaSb [1, 5-6 and references therein]. One of the peculiarities of III-V antimonides is the presence of large concentration of native defects such as vacancies and antisites in as-grown undoped material irrespective of the growth technique [1]. Very limited research has been carried out to understand the effect of the native defects on the electrical and optical properties of these materials. The high below-bandgap absorption has been attributed to optical transitions between the various conduction subbands [7] or transitions from impurity levels [8], mainly native defects. Our effort focused towards obtaining bulk grown low bandgap III-V antimonides with reduced native defects. We have found out that isoelectronic dopants play an important role in determining residual carrier concentrations by compensating native defect thus affecting electrical-optical properties. These properties will be discussed in the paper.

2. Experimental procedure
Crystals of III-Antimonides were grown by the Vertical Bridgman technique in a high pressure multi-zone Mellen furnace. To draw reliable conclusions about the effects of a

* Corresponding author: duttap@rpi.edu
Table 1: Growth Parameters for III-Antimonide crystals

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setup</td>
<td>High Pressure Mullen Furnace</td>
</tr>
<tr>
<td>Crucible</td>
<td>Silica</td>
</tr>
<tr>
<td>Mixing scheme</td>
<td>100 rpm crucible rotation</td>
</tr>
<tr>
<td>Lowering rate</td>
<td>3 mm hour^{-1}</td>
</tr>
<tr>
<td>Pressure</td>
<td>12 psig</td>
</tr>
</tbody>
</table>

parameter, it is imperative that only that parameter should change between a given set of crystals. To ensure that all the crystals grew under the same growth conditions, four small crucibles were stacked up on top of each other inside the reactor chamber, and grown in the same run. The growth parameters are outlined in Table 1. The only difference between these crystals is thus in the choice of dopants. The various iso-electronic dopings in InSb were achieved in the following ways:

1) Ga doping: by introducing GaSb in the melt
2) As doping: by introducing InAs in the melt
3) Ga and As co-doping: by introducing GaAs in the melt

Double sided optically polished wafers were used for the FTIR measurements. The thickness of the samples varied from 1 to 2 mm.

3. Results and Discussion

A variety of long wave infrared materials are commercially available. Transmission curves along with a comparison of the absorption coefficient values are presented in figure 1.

For III-V semiconductors like InSb, there is a presence of a strong absorption edge towards the high photon energies, and a relatively flat region towards the lower photon energies (refer figure 1). In the flat region the dominant absorption mechanism seems to be the free-carrier absorption and it depends on the carrier concentration [4]. Zener – Drude Model is used to model the free carrier absorption for an n-type material wherein it is assumed that since the conduction band in semiconductors is partly filled, just like

![Figure 1: A comparison of various long wave infrared materials.](image)

(Our samples are indicated with RPI as prefix.)
in a metal, the free electron model for a conductor can be applied. The dependence of absorption coefficient, \( \alpha \), on wavelength, \( \lambda \), for n-type semiconductors, is described by

\[
\alpha(\lambda) = \frac{q^3}{4\pi^2c^2m^*\varepsilon_0} \left( \frac{1}{n} \left( \frac{e}{\varepsilon_0} \right)^2 \left( \frac{m^*}{m_n} \right)^2 \right) \left( \frac{N}{\mu} \right) \lambda^2
\]

The terms in the first bracket are physical constants, \( n \) is the refractive index, \( \varepsilon \) is the permittivity, \( m^* \) is the electron effective mass, \( N \) is the free carrier concentration and \( \mu \) is the mobility. In a given material, \( N \) and \( \mu \) can be manipulated by altering growth conditions.

As-grown samples of III-Vs show a large residual carrier concentration. This is attributed to the native defect formation at growth [9]. A group III vacancy and antiasite is known to give rise to p-type behavior, while a group V vacancy and antisite give rise to n-type behavior [10]. As-grown InSb is n-type having a large residual electron concentration which results in a high absorption coefficient. Reduction in \( N \) can be achieved by growing the crystal at a lower temperature. However, for this, growth from non-stoichiometric melts is required. Low temperature growth is not an ideal crystal growth method for In compounds, as excess In sticks to the crucible and retrieval of the crystal becomes tough. Also, mixing becomes an issue in non-stoichiometric melts and the crystals obtained have large number of inclusions. For these reasons, growth at higher temperatures from stoichiometric melts is preferred. In this case, to reduce the residual concentration we require a class of dopants that should compensate the native defects and not give rise to extra free carriers. These requirements are fulfilled by iso-electronic dopants, since iso-electronic dopants do not give rise to charge carriers as they are of the same valency as the constituent lattice atoms and they also tend to compensate for the native defects.

Figure 2 shows the results obtained for the InSb undoped and doped crystals, where samples were intentionally doped with iso-electronic dopants. Table 2 explains the sample nomenclature (used in figure 2), tabulates the various dopant types and lists the calculated absorption coefficients at 9 \( \mu m \).

![Figure 2: FTIR spectra of the InSb wafers (refer Tab 2 for details)](image)
Table 2. Sample nomenclature for figure 2 and calculated absorption coefficients at 9 μm (See text for calculation procedure)

<table>
<thead>
<tr>
<th>Wafer name</th>
<th>Dopant</th>
<th>thickness (mm)</th>
<th>transmission (%) at 9 μm</th>
<th>absorption coefficient (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>None</td>
<td>1.26</td>
<td>12</td>
<td>10.06</td>
</tr>
<tr>
<td>T2</td>
<td>None</td>
<td>1.27</td>
<td>11</td>
<td>10.65</td>
</tr>
<tr>
<td>T3</td>
<td>None</td>
<td>1.29</td>
<td>14</td>
<td>8.65</td>
</tr>
<tr>
<td>T4</td>
<td>Ga &amp; As</td>
<td>1.27</td>
<td>13</td>
<td>9.36</td>
</tr>
<tr>
<td>T5</td>
<td>Ga &amp; As</td>
<td>1.92</td>
<td>12</td>
<td>6.60</td>
</tr>
<tr>
<td>T6</td>
<td>Ga</td>
<td>1.07</td>
<td>14.5</td>
<td>10.12</td>
</tr>
<tr>
<td>T7</td>
<td>Ga</td>
<td>1.35</td>
<td>10</td>
<td>10.72</td>
</tr>
<tr>
<td>T8</td>
<td>As</td>
<td>1.26</td>
<td>19</td>
<td>6.52</td>
</tr>
</tbody>
</table>

The absorption coefficient, \( \alpha \), is related to the transmission, \( T \), by the following,

\[
T = \frac{(1-R)^2 e^{-\alpha l}}{1-R^2 e^{-2\alpha l}}
\]  
(2)

where \( l \) is the sample thickness and \( T \) is the transmission. Reflectivity, \( R \), is given by,

\[
R = \left(\frac{n-1}{n+1}\right)^2
\]  
(3)

where \( n \) is the refractive index. For InSb, \( n \) is taken to be 3.9 between 7 to 15 μm.

From our results, indeed we see a marked relationship between absorption coefficient and the iso-electronic dopant species. Notice that \( \alpha \) goes down (≈6.52 cm⁻¹) with addition of group V element, i.e. Arsenic (sample T8), while it goes up in the presence of a group III element, i.e. Gallium (samples T6 and T7). A simple native defect model can be used to explain why the incorporation of an iso-electronic dopant might increase the transmission significantly. InSb grown at high temperatures i.e. at its freezing point is inherently n-type. At equilibrium, ideally,

\[
In_j + Sb \rightleftharpoons In_j + Sb_h
\]  
(4)

However, in real situations, the melt is slightly In rich as Sb evaporates off from the melt. Thus, we have Antimony vacancies, according to the following equation,

\[
In_j + Sb_h \rightleftharpoons In_j + Sb_{30} + V_{Sb}
\]  
(5)

This vacancy of Antimony can get charged,

\[
V_{Sb} \rightleftharpoons V_{Sb}^+ + e^-
\]  
(6)

leading to n-type behavior of as-grown crystals. Further reactions that are possible are

\[
V_{Sb} + In_j \rightleftharpoons In_j + V_{Sb}
\]  
(7)

and

\[
V_{Sb} + Sb_{30} \rightleftharpoons Sb_{30} + V_{Sb}
\]  
(8)

Although all the native defect species are present in the crystal, it’s the \( V_{Sb} \) and \( Sb_{30} \), that should be dominant, because they are the defect types that can lead to the overall n-type behaviour that is seen experimentally in as grown InSb crystals.

A group V dopant such as Arsenic in InSb, prefers to sit on a group V i.e. on an Antimony site. This fills up the Antimony vacancy and reduces their concentration leading to a reduction in the n-type behavior. Any other n-type dopant that sits on the
Antimony site, other that iso-electronic dopant will give rise to free carriers on account of its valency being different from Antimony, which in turn will increase the free carrier absorption. Once the $V_{\text{As}}$ concentration is reduced, it follows from equations 7 and 8, that $S_{\text{As}}$ concentration will also be reduced. Thus by using an iso-electronic dopant like Arsenic, we are able to achieve compensation of native defects as well as reduction in free carriers.

A group III element e.g. Gallium, increases the vacancy concentration of Antimony. This shifts the equilibrium in equation 5 towards the right, which further increases the total free carrier concentration thereby degrading the transmission characteristics. This can be seen from our results. We see that when As is the sole dopant we have increased transmission, but in the co-doped case, the advantages gained by using As as a dopant are reduced with the presence of Ga in the co-doped sample. This result (refer samples T4 and T5) verifies our explanation.

However, here the reader should be warned of extending this argument to alloy concentrations of InGaSb. When Gallium is present in trace quantities it does not affect the bulk material parameters significantly e.g. the intrinsic carrier concentration, shape of the conduction band, etc. These factors are very different for ternary alloys than their constituent binaries and they play a major role in determining the transmission through a material sample. Our results on transmission through ternaries (InGaSb) will be published elsewhere.

4. Conclusion

We have grown low bandgap antimonides with high transparency in the mid IR wavelength regime by native defect engineering. Binary antimonides grown from stoichiometric melts at high temperatures, doped with iso-electronic dopants can affect the transmission to a great extent. Excellent transmission in InSb has been achieved using this technique. An explanation of this phenomenon is presented using a simple native defect compensation model. Future work, based on this, is directed towards optimizing the dopant concentration required to get the lowest absorption coefficient in binaries and application in growth of ternary antimonides, results of which will be published elsewhere.

References
