Recent advances in nonsilica fiber technology have prompted the development of suitable materials for devices operating beyond 1.55 μm. The III–V ternaries and quaternaries (AlGaIn)(AsSb) lattice matched to GaSb seem to be the obvious choice and have turned out to be promising candidates for high speed electronic and long wavelength photonic devices. Consequently, there has been tremendous upthrust in research activities of GaSb-based systems. As a matter of fact, this compound has proved to be an interesting material for both basic and applied research. At present, GaSb technology is in its infancy and considerable research has to be carried out before it can be employed for large scale device fabrication. This article presents an up to date comprehensive account of research carried out hitherto. It explores in detail the material aspects of GaSb starting from crystal growth in bulk and epitaxial form, post growth material processing to device feasibility. An overview of the lattice, electronic, transport, optical and device related properties is presented. Some of the current areas of research and development have been critically reviewed and their significance for both understanding the basic physics as well as for device applications are addressed. These include the role of defects and impurities on the structural, optical and electrical properties of the material, various techniques employed for surface and bulk defect passivation and their effect on the device characteristics, development of novel device structures, etc. Several avenues where further work is required in order to upgrade this III–V compound for optoelectronic devices are listed. It is concluded that the present day knowledge in this material system is sufficient to understand the basic properties and what should be more vigorously pursued is their implementation for device fabrication.
material because its lattice parameter matches solid solutions of various ternary and quaternary III–V compounds whose band gaps cover a wide spectral range from ~0.3 to 1.58 eV, i.e., 0.8–4.3 μm, as depicted in Fig. 1. Also, detection of longer wavelengths, 8–14 μm, is possible with intersubband absorption in antimonide based superlattices. These have stimulated a lot of interest in GaSb for basic research as well as device fabrication. Some of the important material properties of GaSb are listed in Table I.

From device point of view, GaSb based structures have shown potentiality for applications in laser diodes with low threshold voltage, photodetectors with high quantum efficiency, high frequency devices, superlattices with tailored optical and transport characteristics, booster cells in tandem solar cell arrangements for improved efficiency of photovoltaic cells and high efficiency thermophotovoltaic (TPV) cells. Interestingly, the spin-orbit splitting of the valence band is almost equal to the energy band gap in GaSb leading to high hole ionization coefficients. This results in significant improvement in the signal-to-noise ratio at λ > 1.3 μm in GaAlSb avalanche photodetectors grown on GaAs. GaSb is also predicted to have a lattice limited electron mobility greater than GaAs making it of potential interest in the fabrication of microwave devices. InGaSb has been proposed as an ideal material for transferred-electron devices by Hilsum and Rees with a low threshold yield and a large velocity peak-to-valley ratio, using a Monte Carlo simulation based on the three-level model.

GaSb-based devices are promising candidates for a variety of military and civil applications in the 2–5 and 8–14 μm regimes: to mention a few, infrared imaging sensors for missile and surveillance systems (focal plane arrays), fire detection and monitoring environmental pollution. The absorption wavelengths of several industrial gases and water vapour lie in the near IR range for which GaSb based alloys are suitable. Gas purity monitoring and trace moisture detection in corrosive gases like HCl in semiconductor processing, detecting microleaks of toxic gases such as PH3, in situ monitoring of plasma etching, detecting hazardous gases like HF and H2S in chemical plants, monitoring green house gas fluxes, measurements of flame species in microgravity com-
TABLE I. Material properties of GaSb (compiled from Ref. 5).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>6.0959</td>
</tr>
<tr>
<td>Density (gm cm$^{-3}$)</td>
<td>5.6137</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>985</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>266</td>
</tr>
<tr>
<td>Coefficient of thermal expansion ($10^{-6}$ °C$^{-1}$)</td>
<td>7.75</td>
</tr>
<tr>
<td>Thermal conductivity at 300 K (W cm$^{-1}$ K$^{-1}$)</td>
<td>0.39</td>
</tr>
<tr>
<td>Direct energy gap at 300 K (eV)</td>
<td>0.725</td>
</tr>
<tr>
<td>Direct energy gap at 0 K (eV)</td>
<td>0.822</td>
</tr>
<tr>
<td>Temperature dependence of minimum energy gap ($\times 10^{-4}$ eV K$^{-1}$)</td>
<td>4.2</td>
</tr>
<tr>
<td>Spin-orbit splitting energy, $\Delta_0$ (eV)</td>
<td>0.80</td>
</tr>
<tr>
<td>Effective mass of electrons (in units of $m_0$)</td>
<td>0.0412</td>
</tr>
<tr>
<td>Effective masses of holes (in units of $m_0$)</td>
<td></td>
</tr>
<tr>
<td>Heavy hole mass</td>
<td>0.28</td>
</tr>
<tr>
<td>Light hole mass</td>
<td>0.05</td>
</tr>
<tr>
<td>Spin-orbit split mass</td>
<td>0.13</td>
</tr>
<tr>
<td>Wave number of LO phonons (cm$^{-1}$)</td>
<td>233.0</td>
</tr>
<tr>
<td>Wave number of TO phonons (cm$^{-1}$)</td>
<td>224.0</td>
</tr>
<tr>
<td>Refractive index (near band-gap energy)</td>
<td>3.82</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>15.69</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>14.44</td>
</tr>
<tr>
<td>Elastic compliances ($\times 10^{-12}$ cm$^2$ dyn$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>$S_{11}$</td>
<td>1.582</td>
</tr>
<tr>
<td>$S_{12}$</td>
<td>-0.495</td>
</tr>
<tr>
<td>$S_{44}$</td>
<td>2.314</td>
</tr>
<tr>
<td>Deformation potential constants</td>
<td></td>
</tr>
<tr>
<td>$a$ (eV) (for direct gap)</td>
<td>-8.28</td>
</tr>
<tr>
<td>$b$ (eV)</td>
<td>-2.0</td>
</tr>
<tr>
<td>$d$ (eV)</td>
<td>-4.7</td>
</tr>
</tbody>
</table>

bustion and humidity determination are a few areas where GaSb based alloys might find potential applications. Sodium-based alloys can also find several biological and medical applications in the near IR regime. IR detectors in the 8–14 μm regime based on GaAlSb/AlSb and InAs/InGaSb superlattices and InAsSb are believed to be potential competitors for the present day HgCdTe detectors. GaSb has also proved to be a model material for several basic studies. Because of the band structural properties, GaSb has proved to be an ideal material for studying the Auger recombination processes. Due to low vapour pressures and low melting points, GaSb and InGaSb serve as appropriate model materials to study the effects of convection and diffusion on the solutal distribution under terrestrial and microgravity conditions. Sulfur doped GaSb is the only III–V binary compound which reveals high concentration of donor related deep traps (commonly known as DX centers) at atmospheric pressure. Hence it is the most suitable material for studying the behaviour of such metastable centers without the complication of high pressure or alloy broadening effects, encountered in other III–V binary and ternary alloys. Because of high concentration of native acceptors present in the as-grown unintentionally doped GaSb, it is an interesting system to study impurity compensation effects.

Technological and material aspects of GaSb have sparingly been studied until now, compared to other III–V compounds, such as GaAs, InSb, InP, GaP, etc. Undoped GaSb is always p type in nature irrespective of the growth technique and conditions. Work over the last 3 decades has been devoted mainly for understanding the nature and the origin of the residual acceptors which are the limiting factors for both fundamental studies and device applications. 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 ($Ga_{sb}$) with doubly ionizable nature. Attempts have been made to reduce their content by growing the crystals from nonstoichiometric melts. Recent studies on epitaxial layers of GaSb grown by liquid phase epitaxy and molecular beam epitaxy (MBE) with excess antimony have shown the possibility of reducing substantially the level of natural acceptors and increasing the hole mobility. This stimulated the renewed interest in growth of GaSb crystals with reduced residual acceptors.

At present, GaSb technology is in its infancy and significant progress has to be made both in materials and processing aspects before it can be employed for device applications. Current research and developments are focussed on areas of high quality materials growth, better understanding of electronic and photonic properties and fabrication of suitable device structures. In this article, an overview of the basic physics of the material, preparation and processing technologies, and developments in practical device structures and their properties is presented. Certain avenues where future efforts should be concentrated in order to exploit this III–V compound for optoelectronic devices are suggested.

II. COMPOUND PREPARATION AND CRYSTAL GROWTH

A. Phase equilibria

As early as in 1926, Goldschmidt synthesized GaSb and determined its lattice constant. Since then, it was followed by several workers and the lattice constant was determined more precisely. The phase diagram of this compound has been determined simultaneously by Koster and Thoma and Greenfield and Smith. Later on, the liquidus has been re-evaluated in different regions of the phase diagram by several researchers. The phase diagram and the calculated solidus of GaSb are shown in Figs. 2 and 3, respectively. The melting point of GaSb has been reported to lie between 705 and 712 °C. A melting point depression of less than 50 °C is observed for compositions $\pm 30$ at. % on either side of the stoichiometric composition. Brice and King showed that the liquid–solid–vapour equilibrium temperature is sensitive to pressure—712 °C being the maximum (refer to Fig. 4). The heat of formation and fusion are $-4.97 \pm 0.22$ and 6.0 ± 0.36 kcal/g atom, respectively. The dissociation pressure at the melting point is about $10^{-2}$ mm Hg. Above 370 °C, Sb starts volatilizing from the melt. Thus, GaSb will decompose to yield Sb$_{2}$(v) and GaSb dissolved in liquid Ga. At the maximum melting point, the partial vapour pressure of Sb is $\sim 3 \times 10^{-6}$ Torr. With this partial pressure, up to $2 \times 10^{15}$ Sb atoms per second could be lost from each square centimetre of solid surface. The partial pressure of Ga is less than $10^{-9}$ Torr at the maximum melting point. Thus,
in 10 h run, \( \approx 10^{-3} \) mol of Sb would be lost which amounts to \(~0.1\% \) change in the Sb/Ga ratio. Hence, usually during synthesis of GaSb the Sb/Ga ratio in the melt is taken as 1.001.

On the basis of electrical resistivity measurements, Minomura and Drickamer\(^40\) observed that GaSb undergoes a phase transition around 80–100 kbar at room temperature. The transition was presumed to be structural in nature, although melting could not be discounted. A study of the effect of pressure on the melting point of GaSb by Jayaraman, Klement, and Kennedy\(^41\) in the range 0–65 kbar indicates that the melting temperature decreases by 5 °C per kbar to a triple point near 56.5 kbar and 385 °C. The melting temperature of the high pressure form of GaSb increases 3.4 °C per kbar. The triple point observed by these workers verifies the speculation made by Minomura and Drickamer that the observed transition was solid–solid, but is not in good agreement quantitatively. Later Jamieson\(^42\) verified that the room temperature transition was indeed solid-solid and that the high pressure form is tetragonal Sn type (metallic) with \( \alpha = 5.348 \) Å and \( c = 2.937 \) Å. The transition pressure of 90 kbar observed by Jamieson tends to confirm the pressure transition observed by Minomura and Drickamer. Ozolins \textit{et al.}\(^43\) produced GaSb with excess amounts of the constituent elements and concluded that the lattice parameter is not a function of melt composition. Hence the compound has a very narrow homogeneity range.

B. Bulk growth

The thermophysical properties of molten GaSb at the melting point are listed in Table II.\(^44\) These properties indicate that the growth of low dislocation density crystals is not very difficult.\(^39\) Bulk GaSb crystals have been mainly grown by Czochralski technique (CZ). There are a few reports on Bridgman (BG) technique, travelling heater method (THM), vertical gradient freeze (VGF) technique and liquid phase electro-epitaxy (LPEE). A brief account of crystal growth using these techniques is given below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>6.03 g/cm(^3)</td>
</tr>
<tr>
<td>Thermal conductivity of liquid GaSb</td>
<td>0.171 W/cm K</td>
</tr>
<tr>
<td>Thermal conductivity of solid GaSb</td>
<td>0.0781 W/cm K</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.0231 g/cm s</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>0.328 J/g K</td>
</tr>
<tr>
<td>Volume expansion coefficient</td>
<td>9.58 ( \times 10^{-3} ) K(^{-1})</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>131.16 J/g</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.5</td>
</tr>
<tr>
<td>Thermal diffusivity</td>
<td>0.087 cm(^2)/s</td>
</tr>
<tr>
<td>Prandtl number</td>
<td>0.044</td>
</tr>
</tbody>
</table>

TABLE II. Thermophysical properties of molten GaSb at the melting point (from Ref. 44).
Single crystals of GaSb are usually grown by means of the CZ technique\textsuperscript{39,45–60} (see also references therein). The main problem encountered during growth by early workers was the appearance of a thin oxide film on the GaSb melt surface. The scum has been identified as Ga$_2$O$_3$.\textsuperscript{38} This film impairs the seeding of the melt and promotes twinning during the subsequent growth. To ensure a melt completely free of oxide film, a double-crucible technique\textsuperscript{46} was used. One of the disadvantages of the double-crucible technique was the rather high axial temperature gradient resulting in the formation of many growth twins and dislocations.\textsuperscript{47} The elimination of the oxide was later solved by means of liquid encapsulation of the melt by B$_2$O$_3$. However, the viscosity of the molten B$_2$O$_3$ encapsulant was found to be too high around the melting temperature of GaSb. Later, in order to lower the viscosity, 3.2 mol \% of Na$_3$AlF$_6$ was added to B$_2$O$_3$.\textsuperscript{48} An encapsulant of a mixture of NaCl and KCl (1:1) with a melting point of about 645 °C and a low viscosity in the temperature range of 710–720 °C has also been used.\textsuperscript{49} Growth without any encapsulant but with pure inert gas like N$_2$ or Ar, pure hydrogen and 95% N$_2$:5% H$_2$ have also been used to protect the melt surface against oxidation.\textsuperscript{50} A comparative study on the growth of GaSb single crystals with and without encapsulation had shown that high quality, twin-free crystals were obtained when growth was carried out in hydrogen ambient.\textsuperscript{51} Moreover, crystals grown by this method show higher purity by an order of magnitude in comparison with liquid encapsulated Czochralski (LEC) grown crystals using a B$_2$O$_3$ + Na$_3$AlF$_6$ encapsulant. However, the limitation of this method is the slow reduction kinetics of the Ga$_2$O$_3$ by H$_2$. To overcome this problem, Mo et al.\textsuperscript{53} have adopted an upper–lower crucible technique for \textit{in situ} synthesis and growth of GaSb single crystals. The special feature of this method is that GaSb synthesis is done in the lower crucible in the presence of pure hydrogen and the scum-free melt is transferred to the upper crucible using a sluice gate. Recently, Watanabe and co-workers\textsuperscript{54} have developed a new technique of pulling bulk crystal from Ga solution fed with a GaSb source. Oliviera and Carvalho\textsuperscript{50} have suggested that chemical cleaning of the materials followed by high temperature baking in vacuum can be satisfactorily used to grow crystals from scum-free melts. The diameter of crystals grown by the various workers mentioned above were in the range of 3–5 cm. The pulling and rotation rates employed by them were in the range of 6–12 mm/h and 20–55 rpm, respectively. Typical GaSb crystals grown by the CZ technique show microfacets, impurity striations and twins,\textsuperscript{55,56} although as discussed later twin-free crystals have been grown under special circumstances. Very recently, the Firebird Semiconductors Ltd., Canada have grown GaSb single crystals up to 85 mm in diameter employing the CZ technique.\textsuperscript{57} In addition to growing \textit{p}- and \textit{n}-type GaSb, they claimed to have produced the first commercial high-resistivity GaSb. The resistivity of the crystals at 300 K is 2 × 10$^{-1}$ Ω cm and 4.2×10$^{1}$ Ω cm at 77 K. These values are about twice and 40 000 times, respectively, those of normal undoped material.

### 1. Czochralski technique

Vertical Bridgman growth of GaSb has been reported by relatively few workers.\textsuperscript{14,61–68} Usually crystals are grown in quartz ampoules sealed at 10$^{-6}$ Torr. In earlier works, the ampoule lowering rate employed were in the range of 0.3–1.8 mm/h.\textsuperscript{61,62} Unlike CZ grown crystals, Bridgman grown ones do not exhibit facets and impurity striations and possess better quality. However, this technique has the limitation of the maximum diameter of single crystal that can be grown and has often led to polycrystals.\textsuperscript{64} Roy and Basu\textsuperscript{62} could grow undoped single crystals up to 1 cm diameter. Growth with ampoule diameters less than 0.8 cm or more than 1.1 cm led to polycrystals.\textsuperscript{62} They attributed the occurrence of polycrystallinity to nonuniform heat conduction and wall effect in the case of larger and smaller ampoule diameters, respectively. Sometimes twins were observed near the conical tip at the bottom of the ampoule. The dislocation density in the grown crystals was of the order of 10$^5$ cm$^{-2}$. High dislocation density occurs due to radial heat loss from the ampoule.\textsuperscript{63} By using proper shielding around the ampoule or by enclosing the furnace in vacuum,\textsuperscript{14,64} or by submerging the heater in the melt,\textsuperscript{69} the radial heat flow and thereby the dislocation density can be reduced. In more recent works, it has been demonstrated that high quality single crystals with very low dislocation density (<50 cm$^{-2}$) could be grown by employing a planar melt–solid interface shape.\textsuperscript{14,64–67} A critical ratio of the furnace temperature gradient at the melting temperature $G$ of GaSb to the ampoule lowering rate $V$ has been found to result in planar interface during growth.\textsuperscript{64} It is worth pointing out that low defect content crystals could be grown even with much higher lowering rates (4 mm/h) than that used previously (1.8 mm/h). This was facilitated by the recent theoretical modelling of crystal growth processes in single zone vertical Bridgman furnace.\textsuperscript{66} Extensive studies have further shown that the critical value of $G/V$ for planar interface lies in a narrow range for various experimental conditions as depicted in Fig. 5.\textsuperscript{14,67}

In Bridgman grown crystals without seed, there is no preferential orientation along the growth axis. One of the problems which was encountered by the authors during the Bridgman growth is the improper initial nucleation at the tip of the ampoule due to nonwetting of the melt with the silica ampoules. This often led to polycrystallinity of the grown ingots. The problem has been circumvented by a specific design of the ampoule tip.\textsuperscript{64} Full encapsulation of liquid semiconductors during the Bridgman growth helps to improve the crystal quality by decreasing the nucleations of grains and the dislocation density. Dufar et al.\textsuperscript{64} have recently grown high quality 2-in.-diameter GaSb single crystals in silica crucibles with the LiCl–KCl eutectic (58% LiCl–42% KCl) as full encapsulant. The encapsulant prevents the contact between the sample and the crucible. The wetting of both silica crucible and the semiconductor by this eutectic is extremely good (contact angles practically zero). Moreover, the salts do not contaminate the melt and is of high thermal stability and chemically inert. It can be easily removed from the surface of the crystal after growth.
As far as horizontal Bridgman growth is concerned, very little work seems to have been carried out. The only reported work has been from Lewadowsky et al., who employed the horizontal Bridgman technique to grow single crystals of GaSb. The boat sliding rate employed by them was 11 mm/h. Crystals up to 1.3 cm in diameter and 15 cm in length have been grown. The quality of the bulk crystals was as good as that of epitaxially grown high purity layers.

3. Vertical gradient freeze technique

The VGF technique has been used to grow high quality device grade single crystals of III–V compound semiconductors with very low dislocation density. In the VGF technique, the crucible and the furnace are kept stationary and the growth is achieved by slowly cooling the melt in an appropriate temperature gradient. One of the principal advantages of this technique is the much reduced axial and radial temperature gradients with concomitant advantages of reduced convective flow and thermal stresses. Garandet, Duffar, and Favier used this technique to grow single crystals of GaSb of 1 cm diameter and 5 cm length on 〈111〉-oriented seeds with dislocation density below 100 cm\(^{-2}\). The growth rate was about 3 mm/h. They could grow practically zero dislocation GaSb single crystals in silica crucibles by complete encapsulation with LiCl–KCl eutectic by the VGF technique.

4. Travelling heater method

Only a few reports exist on the growth of GaSb by vertical and horizontal THM. The main advantage of this technique is low growth temperature which reduces vapor pressure problems and stoichiometric native defect concentration. In THM, a solvent zone placed between a solid seed and the feed material is heated and moved by a travelling heater. In this way crystallization takes place at the advancing seed/solvent interface and dissolution of feed material at the solvent/feed phase boundary. The solute transport in the liquid zone may be established by diffusion and/or by convection. As discussed by Benz and Muller, the dislocation density in the crystals grown by this technique can be orders of magnitude lower than in the seed. The growth temperature used was in the range of 500–560 °C. Both Ga and In solvents have been used with zone length in the range of 3–13 mm. The main disadvantage of the THM technique is its low growth rate (~few mm/day). For GaSb, growth rates between 0.7 and 5 mm/day have been achieved. It is principally limited by the transport rate of the slowest constituent species through the solution zone. Moreover, the morphological instability of the growing interface caused by constitutional supercooling limits the maximum growth rate for inclusion-free single crystals. The usage of Ga-rich melts results in dendritic growth and compositional inhomogeneity caused due to fluctuations in the freezing rate at the solid–melt interface. Several workers used uniform rotation, accelerated crucible rotation, rf heating or stirring by alternating magnetic fields to increase the growth rate (see references in Refs. 72 and 73); however, the growth rate merely increased by a factor of 2.

5. Liquid phase electro-epitaxy

The LPEE technique was earlier used by Gevorkyan et al., and recently by Bischopink and Benz to grow bulk GaSb crystals. The growth is carried out in vertical reactor made of graphite and pyrolytic boron nitride. The GaSb source material and the solution zone were stored in the movable upper part of the growth cell which served as cathode. The GaSb substrate was placed in the lower part of the growth cell which forms the anode. When the feed is in contact with the solution zone, the electrical circuit is closed and the growth starts. The mechanism of material transport is principally based on Peltier cooling at the substrate–solution interface and on the electromigration of the dissolved compounds in the solution zone. The growth is mainly governed by electromigration. The Peltier cooling only enhances the growth rate during the early stages of growth. The electrical resistivity of the entire growth system (growth cell, solution zone, substrate and electrical contacts) was such that the amount of joule heating was very low. The growth temperature was varied in the range of 550–575 °C. The current density was in the range of 5–10 A/cm\(^2\). The growth rate was linearly proportional to the current density and was found to vary from 0.4 to 0.8 mm/day. When current density in excess of 5 A/cm\(^2\) was used, local pits of 50–100 μm dimensions were found on the p-type substrate. This is due to the high Peltier heating in p-type material, which entails local dissolution of the substrate. No significant difference in the growth rates of p- and n-type materials was seen proving that the material transport by Peltier cooling is negligible against electromigration.

6. Growth under microgravity

In space at zero gravity, the molten semiconductor does not stick to the quartz wall leading to good surface quality.
The heat transfer in space differs from that in the terrestrial conditions. The vacuum gap between the ingot and the ampoule wall allows only a limited amount of heat to be dissipated from the surface. The heat flows in the axial direction which results in relatively stress free crystals. Lendvay et al.76 were able to grow high quality bicrystals using the Bridgman technique under microgravity conditions (10−5 g). The translational rate of the ampoule was 0.188 mm/min. A crystal with a diameter of 8 mm and length of 39 mm was grown. While the dislocation density, resistivity and carrier concentration were same for both the terrestrial and space grown crystals, the mobility was found to be higher in the latter. The dislocation density was of the order of 105 cm−2. The hole mobility at 77 K was 2700 and 2000 cm2/V s for the space grown and terrestrial grown crystals, respectively. The resistivity and carrier concentration were of the order of 0.12 Ω cm and 1016 cm−3 at 77 K, respectively, for both the crystals. In the past few years, a large number of space experiments has been carried out to study the impurity segregation phenomena in GaSb and InGaSb under microgravity conditions.10 In space, the gravity driven convection in the melt is reduced and diffusion controlled heat and mass transport conditions can be achieved. Under such conditions, it is possible to grow binary and ternary alloys with uniform axial impurity or solutal concentrations, respectively.

7. Growth under hypergravity

Growth of crystals under hypergravity conditions has also been investigated by some workers in recent times.72,77 The high gravitational fields are known to influence the distribution of dopants and crystal morphology.72 The effect of enhanced acceleration on gravitational convection was investigated by Muller and Neumann.72 They had grown GaSb by THM at an acceleration of 20 g using a horizontal centrifuge arrangement. Inclusion-free crystals (at Tm−550 °C) could be grown at growth rate as high as 14 to 20 mm/day, which is nearly one order of magnitude higher than that at normal g. The increase in growth rate is due to the enhanced convection in the solution zone. Doping striations were seen in the crystals similar to that in the case of crystals grown by THM at normal g. This suggests that the striations do not result from unsteady convection caused due to temperature and solute gradients. The striations may be caused by an interface instability mechanism which is independent of the gravity driven convection. Regel and Shumaev77 employed the Bridgman technique coupled with a centrifuge accelerated to 5.2 g for the growth of GaSb with a cooling rate of 1.5 cm/h. The solid–melt interface was found to be planar. No striations were found in the grown crystals; however, twins were found in the upper end of the crystals.

8. Bulk growth of GaSb based ternaries

In recent years, a few groups have investigated the possibility of growing bulk crystals of ternaries like AlGaSb and InGaSb.78–81 The LPEE, Bridgman, THM and VGF techniques have been employed for growth either under microgravity or in terrestrial conditions. The main motivation of these studies is to grow crystals with uniform radial and axial compositions. For this purpose, the effects of convection and diffusion on the composition of the grown crystals were studied. A great deal of effort has been made to eliminate the problem of initial and final solutal transients by growing the crystals with preestablished solutal concentration profiles in the polycrystalline feed. The morphological instability with increasing Al and In content in the melt has been studied both theoretically and experimentally.

The binary compounds GaSb and InSb are totally miscible, both in liquid and in solid state, thereby allowing for the physical properties of the InGaSb alloy to vary continuously with the InSb composition.82 The equilibrium phase diagram in the GaSb–InSb quasibinary section of the GaInSb system is shown in Fig. 6.83 During the solidification of InGaSb, there is a rejection of solute molecules (InSb) by the solid into the liquid. The rejected material accumulates in front of the interface and spreads into the liquid phase, by diffusion and mixing induced by convection, which in turn is dependent on the growth conditions. Joullie, Allegre, and Bougnot84 studied the structural and compositional properties of directionally solidified InGa1−xSb with homogeneous starting charge with x = 0.8. Polycrystalline ingots were obtained with grain structure continuously changing along the growth direction due to variation in crystal composition by segregation. The homogeneity of the material is highly dependent on the crystallization rate. For example, while crystallization up to 1 mm/h gives radially homogeneous samples, the rates above this result in a second phase (in the form of inclusions) in the nearly homogeneous matrix. One of the technical difficulties encountered by early workers is the long time required for reaching equilibrium of this compound when prepared from powdered starting substances. Extremely long mixing times of the order of several hundreds of hours was found to be insufficient to prepare this compound in homogeneous form. Another major problem is

FIG. 6. Pseudobinary phase diagram of InSb–GaSb. The lines are theoretically calculated curves and the symbols are experimental data (from Ref. 85).
the sticking of the material to quartz ampoule (due to unreacted indium and its oxide) and ampoule cracking during homogeneization and growth which limits the utility of the grown crystals. Using a critical high temperature baking cycle prior to homogeneization, the problem of sticking and cracking has been solved and homogeneous mixture of In$_{0.2}$Ga$_{0.8}$Sb could be prepared. Garandet and co-workers could grow reasonably good quality single crystals up to 5% of InSb with uniform radial composition by the VGF technique. By carrying out growth at low temperatures, the native acceptor concentration could be reduced to a level of 10$^{16}$ cm$^{-3}$. The Sb-rich melt is the most effective solution for reducing the native acceptor concentration; however, growth from Sb-rich solutions is limited by the eutectic point in the Ga–Sb phase diagram at $T = 588.5 \, ^\circ C$ for 0.884 atom fraction of Sb. Woelk and Benz have grown undoped $p$ epilayers from Ga- and Sb-rich solutions in the temperature range of 330–470 and 635–680 °C, respectively.

In recent studies on surface morphology and electrical and optical properties of GaSb layers, it has been found that the growth temperature range of 500–550 °C with Ga melt is optimal for obtaining high quality layers with excellent surface morphology. Typical morphology of an epilayer grown from Ga-rich melts at 550 °C is shown in Fig. 8a. Even though the epilayers grown at low temperatures possess low native defect concentration, they exhibit poor morphology and hence are not suitable for device applications. Similarly, the Sb-rich melt, even though it efficiently reduces the native defect content, results in faceted growth which is again undesirable for device applications. The luminescence efficiency for layers grown from Sb-rich solutions was less compared to those grown from Ga-rich solutions. This has been attributed to higher contamination of impurities which is expected for high growth rates in the case of Sb-rich solutions. By carrying out growth from a two phase solution technique, abrupt $p-n$ junctions with epilayer thickness $\sim 1 \, \mu m$ have been obtained.

C. Epitaxial growth

Epitaxial growth of GaSb has been largely carried out by liquid phase epitaxy (LPE). A few reports exist on vapour phase epitaxy (VPE), chemical vapour deposition (CVD), metal-organic chemical vapour deposition (MOCVD), MBE, metal organic molecular beam epitaxy (MOMBE) and plasma assisted epitaxy (PAE). The details are discussed below.

1. Liquid phase epitaxy

There exist quite a few reports on growth of GaSb by LPE technique. Ga-, Sb-, Sn- and Bi-rich melts have been used for the growth in the temperature range of 330–680 °C. By carrying out growth at low temperatures, the native acceptor concentration could be reduced to a level of 10$^{16}$ cm$^{-3}$. The Sb-rich melt is the most effective solution for reducing the native acceptor concentration; however, growth from Sb-rich solutions is limited by the eutectic point in the Ga–Sb phase diagram at $T = 588.5 \, ^\circ C$ for 0.884 atom fraction of Sb. Woelk and Benz have grown undoped $p$ epilayers from Ga- and Sb-rich solutions in the temperature range of 330–470 and 635–680 °C, respectively.

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Chandvankar and Arora have carried out dissolution studies of GaSb in Sn solution and grown undoped epilayers. Bi melts have been used by a few workers in the growth temperature range of 390–550 °C. Recently, Gladkov and
co-workers\textsuperscript{91} employed Bi-rich melts for the growth of undoped GaSb. A native acceptor concentration of \(\sim 10^{16}\) cm\(^{-3}\) could be obtained. Photoluminescence studies revealed the incorporation of approximately 0.015 at % Bi in the grown epilayers. This resulted in reduction of band gap by 0.8 meV. Nevertheless, Bi was found to be electrically inactive.

For \(n\)-type layers, Te doping has been carried out.\textsuperscript{88,92,93} Capasso and co-workers\textsuperscript{88} could achieve very low net donor concentration in the range of \(10^{14}–10^{15}\) cm\(^{-3}\) from undoped Ga-rich solutions in the 300–375 °C range and by Te compensation using Ga-rich melt at 500 °C. Miki and co-workers\textsuperscript{94} were also able to grow undoped \(n\)-type layers at 400 °C from Ga-rich melt with net donor concentration of \(\sim 10^{15}\) cm\(^{-3}\) and mobility as high as 7700 cm\(^2\)/V s. In our studies we have observed that undoped layers grown from antimony-rich melts always exhibit \(p\)-type conductivity irrespective of the growth temperature.\textsuperscript{95} In contrast, a type conversion from \(p\) to \(n\) was observed in layers grown from Ga-rich melts below 400 °C.\textsuperscript{96}

Secondary ion mass spectrometry (SIMS) analysis of GaSb grown by LPE technique usually shows unintentional impurities, C, Si and O, which are acceptors in GaSb. The carbon comes from the graphite boat that is used for the growth and Si from the quartz tube. Oxygen is usually a donor in III–V, but may form an acceptor complex. Oxygen incorporation can take place from microleaks in the system. The concentration of these impurities depends on the bake-out duration of the melt prior to growth. Although pileup impurities are detected at the epilayer–substrate interface, there is no correlation between hole concentrations and these impurities, implying that the background carrier concentration originates from native defects.

2. Vapour phase epitaxy

Vapour growth of GaSb is difficult because the equilibrium vapour pressure of antimony is extremely low and hence the transport rate or the growth rate of GaSb is usually very small. A few workers\textsuperscript{97–101} have succeeded in the epitaxial growth of GaSb by VPE. Arizumi and co-workers\textsuperscript{100} carried out epitaxial growth of GaSb on GaAs substrates in open tube system by reacting a mixture of SbH\(_3\) and HCl gases with metallic Ga. They have also used a closed tube system with polycrystalline GaSb as the source material and HCl, SbCl\(_3\) and I\(_2\) as transporting agents. The growth rates were found to range from 0.5 to 10 \(\mu\)m/h when the initial amount of the transport agent in the charge was from \(10^{-8}\) to \(10^{-6}\) mol/cm\(^2\). The surface morphology of the grown layers was found to depend on the substrate temperature and the amount of vapour etching done prior to growth. Smooth layers were obtained for growth temperatures higher than 600 °C with 30 min of vapour etching prior to growth. The minimum hole concentration in the undoped layers was found to be \(1.5 \times 10^{16}\) cm\(^{-3}\) with a mobility larger than 700 cm\(^2\)/V s. Layers grown using HCl gas as the transport agent usually show nonuniform distribution of acceptors which presumably come from water vapour contained in the HCl gas. When carefully dried HCl gas was used, the hole concentration decreases to the level of \(10^{16}\) cm\(^{-3}\), which corresponds to the native acceptor concentration.

CVD growth of GaSb has been reported by Jakowetz et al.\textsuperscript{102} MOCVD growth of GaSb has been carried out\textsuperscript{103–110} using trimethylgallium (TMGa) or triethylgallium (TEGa) and a host of Sb-containing metal-organic precursors in the temperature range of 450–625 °C. From these studies, tris-dimethylaminoantimony (TDMA\textsubscript{Sb}) has been found to be an excellent precursor for the MOVPE growth over a wide range of growth temperatures.\textsuperscript{104} The optical and electrical properties of layers grown by the CVD and MOCVD techniques are similar to that of layers grown by the VPE technique. The main source of background impurities during MOCVD growth comes from the carbon during pyrolysis of TMGa or TEGa, yielding high concentration of unintentional acceptors. TESb and TMSb decompose insufficiently at low temperatures and need to be thermally precracked at high temperatures. However, in spite of the residual carbon contamination, the dominant acceptors have been found to be the native defects. The TDMA\textsubscript{Sb} is expected to produce low carbon contamination due to the absence of direct Sb—C bonds and effective decomposition at low temperatures (300 °C).

3. Molecular beam epitaxy

The main difficulty in growing GaSb by MBE is again the low vapour pressure of antimony.\textsuperscript{111} As a result, during crystal growth Sb will have a low surface mobility and tend to aggregate together forming clusters and precipitates. This leads to vacant Sb sites. Thus, antiseite defects like Ga\textsubscript{Sb} are formed. Therefore, to improve the quality of MBE grown layers, an Sb-rich environment is needed. One can achieve this by using proper orientation of the substrate like (311)\textsubsymbol{B}, (111)\textsubsymbol{B}, etc. Longenbach and Wang\textsuperscript{20} used (311)\textsubsymbol{B} oriented substrates to reduce the native \(p\)-type centres in the grown layers. Usually the growth rate varied from 0.6 to 2.5 \(\mu\)m/h for the growth temperatures in the range of 500–600 °C. Very low acceptor concentration \((\sim 10^{15}\) cm\(^{-3}\)) could be obtained using this approach. Undoped GaSb epilayers have shown C, O and Si impurities. The origin of these impurities can vary from one growth system to another and can be due to different sources.

Generally, Te doping is accomplished in MBE grown layers by the use of a PbSe cell since this provides better control of temperature than the use of elemental Te.\textsuperscript{112} There appears to be a trace incorporation of Pb in the grown layer. Donor concentrations of above \(10^{18}\) cm\(^{-3}\) are readily obtained. Other compounds that may be used for Te doping are GaTe, SbTe, GeTe and SnTe.\textsuperscript{113–118} Selenium doping from a PbSe cell\textsuperscript{119} and sulfur doping from a Ag\textsubscript{2}S electrochemical cell\textsuperscript{120} have also been carried out. The \(p\)-type conductivity may be accomplished by Ge, Sn or Be doping in the MBE process.\textsuperscript{3} The covalent radius of Sb (1.4 Å) is larger than that of Ga (1.25 Å) and therefore group IV atoms tend to occupy the Sb sites. Sn (1.40 Å) is a larger atom than Ge (1.22 Å) and consequently, it is more difficult to achieve heavy doping with Sn. Silicon being a small atom gets dis-
tributed amongst the two sites and the compensation ratio is high. Hence, Si is not generally used as a p-type dopant.

4. Metal-organic molecular beam epitaxy

MOMBE growth of GaSb and InAsSb has been carried out using TEGa, TEIn, TESb and TEAs. The maximum growth rate of GaSb is observed at a substrate temperature of 500 °C. Recently, MOMBE growth and etching of GaSb on flat and high index surfaces using TDMASb, as well as elemental antimony Sb, and TEGa have been reported by Yamamoto et al. When only TDMASb is supplied, GaSb surfaces are etched for all misoriented substrates and native oxide could be removed at 540 °C. On the other hand, when TEGa is simultaneously supplied in addition to TDMASb, the surface reaction is changed from etching to growth on the surface. The growth rate is typically 1 \mu m/h at 500 °C. A growth temperature in the range of 450–570 °C was used. Good surface morphology across a range of 1:3 to 1:6. The maximum growth rate of GaSb is observed at a substrate temperature of 25.15 °C at a growth temperature of 900 °C. A growth rate of 1–2 \mu m/h is found to be 6.0958 82 Å, 3.4963 \times 10^{-5} Å °C^{-1}, 3.3456 \times 10^{-8} Å °C^{-2}, -4.6309 \times 10^{-11} Å °C^{-3} and 2.6369 \times 10^{-14} Å °C^{-4}, respectively.

Where: $T$ is the temperature in °C. The values of the constants $a_0$, $a_1$, $a_2$, $a_3$ and $a_4$ are 6.0958 82 Å, 3.4963 \times 10^{-5} Å °C^{-1}, 3.3456 \times 10^{-8} Å °C^{-2}, -4.6309 \times 10^{-11} Å °C^{-3} and 2.6369 \times 10^{-14} Å °C^{-4}, respectively.

5. Plasma assisted epitaxy

The low temperature epitaxial growth of GaSb in hydrogen plasma was reported by Sato et al. This process has several advantages, such as cleaning effect of the substrate surface by sputtering or by plasma etching, efficient impurity doping, high growth rate, good surface morphology across a large area and reduced stoichiometric defects due to low growth temperatures. Growth was carried out using TEGa, TEIn, TESb and TEAs. The maximum growth rate of GaSb is observed at a substrate temperature of 900 °C. A growth rate of 1–2 \mu m/h is found to be 6.0958 82 Å, 3.4963 \times 10^{-5} Å °C^{-1}, 3.3456 \times 10^{-8} Å °C^{-2}, -4.6309 \times 10^{-11} Å °C^{-3} and 2.6369 \times 10^{-14} Å °C^{-4}, respectively.

B. Density

The density of GaSb at 300 K is measured to be 5.6137 g cm^{-3}. There is very little variation of density with temperature. At 900 K, it is found to be 5.60 g cm^{-3}.

C. Crystal structure

GaSb crystallizes in zinc-blende structure, which belongs to the space group $F43m$ in the Hermann–Mauguin notation, or $D_{4h}^5$ in the Schoenflies notation. The zinc-blende structure is identical to that of the diamond lattice except that each Ga atom has four tetrahedrally arranged Sb neighbours and vice versa. Unlike the diamond structure, the zinc-blende structure does not possess a centre of inversion, and opposite directions in the crystal are not necessarily equivalent. This leads to interesting arrangements of the atoms in the (110), (100) and (111) planes. The (100) surfaces are stepped and contain both Ga and Sb atoms. The nature of chemical bonds in III–V compounds are of mixed covalent-ionic type. The ionicity of GaSb is 0.33. The presence of a slight ionic component in the bonds and the fact that there are equal numbers of Ga and Sb atoms on the (110) planes results in the (110) cleavage of the compound. The zinc-blende lattice structure and partial ionic bonding impart to the crystal a polarity along the [111] axis. The (111) planes can be prepared with either Ga or Sb atoms on the surface. The (111) plane composed of Ga atoms is designated as (111)A. The (1,1,1) plane is composed of Sb atoms and is designated as (111)B. These two surfaces exhibit striking differences in their chemical, electrical and mechanical properties.

From high pressure Raman studies at 300 K, it has been found that above 7.65 GPa, a white tin structure with space group $D_{4h}^{19}$ results. 127

IV. THERMAL PROPERTIES

A. Heat capacity and Debye temperature

Very few measurements of heat capacity are available in the literature for GaSb. Piesbergen measured the values of $c_p$, $c_v$ and $\Theta$ for GaSb in the temperature range of 12–273 K. For temperatures in the range 20–700 °C, $c_p$ can be expressed as:

$$c_p = 0.04351 + (4.635 \times 10^{-5}) T\text{ cal/g deg},$$

where $T$ is the temperature in °C. The value of $c_p$ at 298 K is 0.06058 cal/g deg. The temperature dependence of specific heat $c_v$ is shown in Fig. 9.

The plot of Debye temperature $\Theta$ versus temperature is shown in Fig. 10. As can be seen from the figure, the $\Theta$ runs through a minimum at low temperatures. This minimum is in agreement with the results from the lattice absorp-
tion bands in the infrared, which give a relatively low energy for the transverse acoustic phonons.\textsuperscript{131,132} The decrease in \( \Theta \) at higher temperatures is believed to be due to anharmonic effects in the lattice vibrations. In order to give an estimate of this contribution, a parameter \( \Theta_\infty \) is calculated from Thirring expansion. This value for GaSb is 316 K. At very low temperatures, where only the low frequencies contribute to atomic heat, the value of \( \Theta \) is calculated to be 266 K.\textsuperscript{133–135}

B. Elastic moduli and phonon dispersion

The measurements of the elastic properties of the III–V compounds have so far been mainly confined to the determination of the three second-order constants. The second-order elastic moduli versus temperature plots for GaSb obtained using ultrasonic technique\textsuperscript{136} are shown in Fig. 11. The values of elastic moduli, \( c_{11}, c_{44} \) and \( c_{12} \) (in \( 10^{11} \) dyn cm\(^{-2}\)) at 296 K are 8.834, 4.322 and 4.023, respectively.

The phonon dispersion relations are shown in Fig. 12. The experimental points are obtained from inelastic neutron scattering experiments.\textsuperscript{137} The continuous curves are obtained from the parameter shell model calculation. From first-order\textsuperscript{127} and second-order\textsuperscript{138} Raman scattering experiments at 300 K, the phonon wave numbers (in cm\(^{-1}\)) obtained are indicated below

\[
\begin{align*}
\bar{\nu}_{\text{TO}}(\Gamma) & : 223.6, \quad \bar{\nu}_{\text{LO}}(\Gamma) : 232.6, \\
\bar{\nu}_{\text{TA}}(L) & : 46, \quad \bar{\nu}_{\text{TA}}(X) : 56, \\
\bar{\nu}_{\text{TA}}(W) & : 75, \quad \bar{\nu}_{\text{LA}}(L) : 155, \\
\bar{\nu}_{\text{LO}}(L) & : 204, \quad \bar{\nu}_{\text{LO}}(X) : 210, \\
\bar{\nu}_{\text{TO}}(L,X,S) & : 218.
\end{align*}
\]

Fig. 13 shows the Raman spectra of GaSb taken for the 5309 Å line at various pressures.\textsuperscript{127} With increasing pressure, the LO and TO phonons shift to higher frequencies and their
peak heights also vary. The intensities of phonon peaks increase with pressure, go through a maximum and then decrease. The transition to the metallic phase occurs at 7.65 GPa. The shifts of the phonon frequencies with relative lattice constant ($-\Delta a/a$) and pressure are shown in Fig. 14.127

C. Thermal expansion

The linear thermal expansion coefficient $\alpha$ for GaSb in the temperature range 25–340 K is shown in Fig. 15.139 As can be seen from the figure, $\alpha$ is negative for temperatures less than 0.20. For cubic structures, the volume coefficient of thermal expansion $\beta$ is equal to $\alpha$.

The thermal expansion of GaSb above room temperature has been investigated by Bernstein and Beals.140 The temperature dependence of the relative expansion is shown in Fig. 16. As can be seen from the figure, a sharp deviation from linearity is observed in the interval 300–400 °C, and it was impossible to make measurements beyond 436 °C.

The temperature dependence of Gruneisen parameter $\gamma$ for GaSb is shown in Fig. 17.141 Near the Debye temperature $\gamma$ is independent of temperature. At low temperatures $\gamma$ has a region of negative values which coincides with the region in which the expansion coefficient is negative. The temperature at which $\gamma$ changes sign coincides with the temperature at which $\alpha$ also changes sign.

D. Thermal conductivity

The thermal conductivity as a function of temperature for four GaSb samples ($p$ and $n$ type) is shown in Fig. 18.142,143 The shape of the curves is similar to that obtained theoretically for III–V compounds by considering the contri-
butions from various scattering processes like crystalline boundaries, impurities, three-phonon, four-phonon, resonance and electron–phonon scattering; however, it should be noted that the experimental data showed a change in slope at low temperatures for the $p$-type samples. As can be seen from the figure, even though the $n$-type samples contain 10 times more impurity than the $p$-type samples, they possess a higher value of $\kappa$ for most of the low temperature region. Theoretically calculated thermal conductivity at low temperatures (up to 10 K) in the boundary scattering region overestimates the experimental data by almost a factor of 100. An attempt was made to fit the data using an analysis due to Ziman\textsuperscript{144} which treats scattering of phonons by electrons in a degenerate band. While the magnitude of the thermal conductivity is correctly predicted, this scattering does not account for the change in slope in the $p$-type material nor can it account for the dependence on impurity concentration. Further, by using the electron–phonon mechanism suggested by Keyes\textsuperscript{145} an attempt was made to fit the data.\textsuperscript{146} In this case, the scattering is due to the strain sensitivity of the donor (or acceptor) ground-state energy. The change in slope near 5 K could be obtained in the analysis.

The high temperature lattice thermal conductivity of GaSb is shown in Fig. 19.\textsuperscript{147} The decrease in $\kappa$ with increasing free carrier concentration is attributed to scattering of phonons by electrons. Some optical phonon scattering has also been identified. Steigmeier and Kudman\textsuperscript{147,148} have evaluated the influence of optical mode scattering on the lattice thermal conductivity of group IV and III–V semiconductors. Using the values of $M_1/M_2$, $M$, $\Theta$ and $\kappa$, they calculated the Gruneisen anharmonicity parameter. The values of each of these quantities for GaSb are listed below.

\[ M_1/M_2 \text{ (atomic mass ratio)}: 1.75, \]
\[ M \text{ (mean atomic mass)}: 95.7, \]
\[ \Theta \text{ (Debye temperature in K)}: 265.5, \]
\[ \kappa \text{ (at } T=0 \text{ K in W/cm deg)}: 0.390, \]
\[ \gamma \text{ (at } T=\Theta) : 0.86. \]

The large value of $\gamma$ for GaSb implies significant scattering by the optical mode.

The thermal conductivity of GaSb has also been investigated in the presence of magnetic field in the low temperature region, however it has been found to be independent of the magnetic field.\textsuperscript{130}
V. ELECTRONIC AND TRANSPORT PROPERTIES

A. Band structure

Fig. 20 shows the band structure of GaSb obtained with a nonlocal pseudopotential calculation. The symmetry symbols are in double group notation. The conduction band is characterized by three sets of minima. The lowest minimum is at \( \Gamma \). The next higher minima are the \( L \) points at the surface of the Brillouin zone and at the \( X \) points. The valence band has the structure common to all zinc-blende semiconductors. The energies of the symmetry points of the band structure relative to the top of the valence band (in eV) are given in Table III. The first column gives the theoretically calculated values, the second column is obtained from the ARPES data, and the third column is the electroreflectance data (EL) at 10 K.

Using photoluminescence spectroscopy at 2 K, the excitonic gap \( E_{\text{g},x} \) has been found to be 0.8099 eV. Assuming an exciton binding energy of 1.4 meV, the direct band gap \( E_{\text{g},\text{dir}} (\Gamma_6 - \Gamma_6) \) was evaluated to be 0.8113 eV. The extrapolated band gap at 0 K was found to be 0.822 eV from the electroreflectance experiment as shown in Fig. 21. The band gap at 300 K is 0.725 eV. The values of constants \( \alpha \) and \( \beta \) used in the equation for evaluating the band gap at various temperatures from the band gap at 0 K are 4.2 \( \times 10^{-4} \) eV K\(^{-1}\) and 140, respectively.

The direct gap energies calculated from interband direct Faraday rotation are 0.74 and 0.82 eV at 296 and 77 K, respectively.

The pressure dependence of the absorption edge is given below:

\[
\frac{dE_g}{dP} = -1.2 \times 10^{-6} \text{ eV/kg/cm}^2 \quad \text{for} \quad P \leq 18000 \text{ kg/cm}^2,
\]

\[
\frac{dE_g}{dP} = 7.3 \times 10^{-6} \text{ eV/kg/cm}^2 \quad \text{for} \quad 18000 \text{ kg/cm}^2 \leq P \leq 45000 \text{ kg/cm}^2,
\]

\[
\frac{dE_g}{dP} = \text{negative for} \quad P \geq 45000 \text{ kg/cm}^2.
\]

At normal pressures, the (000) band lies lowest, followed by the (111) and then (100) bands. The minima assigned to the above three pressure ranges are (000), (111) and (100), respectively.

The critical point and spin-orbit splitting energies (in eV) as measured from modulation spectroscopy at 27 K are given below.

<table>
<thead>
<tr>
<th>Symmetry points</th>
<th>Theory</th>
<th>ARPES</th>
<th>EL</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E(\Gamma_6) )</td>
<td>-12.00</td>
<td>-11.64</td>
<td>-0.756</td>
</tr>
<tr>
<td>( E(\Gamma_7) )</td>
<td>-0.76</td>
<td>-0.82</td>
<td>-0.756</td>
</tr>
<tr>
<td>( E(\Gamma_8) )</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E(\Gamma_9) )</td>
<td>0.86</td>
<td>0.822</td>
<td></td>
</tr>
<tr>
<td>( E(\Gamma_{10}) )</td>
<td>3.44</td>
<td>3.191</td>
<td></td>
</tr>
<tr>
<td>( E(\Gamma_{11}) )</td>
<td>3.77</td>
<td>3.404</td>
<td></td>
</tr>
<tr>
<td>( E(\Gamma_{12}) )</td>
<td></td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>( E(L_{6a}) )</td>
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<td>-10.06</td>
<td></td>
</tr>
<tr>
<td>( E(L_{6b}) )</td>
<td>-6.25</td>
<td>-6.60</td>
<td></td>
</tr>
<tr>
<td>( E(L_{6c}) )</td>
<td>-1.45</td>
<td>-1.55</td>
<td>-1.530</td>
</tr>
<tr>
<td>( E(L_{6d}) )</td>
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<td>-1.10</td>
<td></td>
</tr>
<tr>
<td>( E(L_{6e}) )</td>
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<td>( E(L_{6f}) )</td>
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<td>4.36</td>
<td></td>
</tr>
<tr>
<td>( E(L_{6g}) )</td>
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</tr>
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<td>( E(\Gamma_{8a}) )</td>
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</tr>
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<td>( E(\Gamma_{8b}) )</td>
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</tr>
<tr>
<td>( E(\Gamma_{8c}) )</td>
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</tr>
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<td>( E(\Gamma_{8d}) )</td>
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</tr>
<tr>
<td>( E(\Gamma_{8e}) )</td>
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<td>( E(\Gamma_{8f}) )</td>
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<td></td>
</tr>
<tr>
<td>( E(\Sigma_{34e}) )</td>
<td></td>
<td>-3.64</td>
<td></td>
</tr>
<tr>
<td>( E(\Sigma_{34f}) )</td>
<td></td>
<td>-3.90</td>
<td></td>
</tr>
</tbody>
</table>
\[ E_0 + \Delta_0 = (\Gamma_{7e} - \Gamma_{6c}) = 1.569, \]
\[ E_1 = (L_{4.5e} - L_{6c}) = 2.185, \]
\[ E_1 + \Delta_1 = (L_{6e} - L_{6c}) = 2.622, \]
\[ E_L = (\Gamma_{8e} - L_{6c}) = 0.871. \]

The intraconduction band energy difference between the lowest conduction band minimum \((\Gamma_{6e})\) and the lowest \(L\) band minimum \((L_{6e})\) was found to be 61 and 82 meV at 300 K employing Hall and magnetoresistance measurements.\(^{156}\)

The two values have been obtained by assuming the effective mass of electron in \(L\) band to be 0.22\(m_0\) and 0.43\(m_0\), respectively. The energy difference between the \(\Gamma\)-band minimum and the \(X\)-band minimum was found to be 430 meV at 10 K using the electroreflectance technique.\(^{151}\)

The camel's back structure of conduction band edge was estimated from the \(k \cdot p\) theory using the GaP data.\(^{157}\)

The values of various camel's back parameters are tabulated below

\[ \Delta:178 \text{ meV}, \]
\[ \Delta E:25.1 \text{ meV}, \]
\[ k_m:0.127(2\pi/\alpha), \]
\[ m_t:0.250m_0, \]
\[ m_c:1.2m_0. \]

The electron \(g\) factor at 30 K calculated using stress modulated magnetoreflectance has been evaluated to be \(-7.8.\)^{158}

Molar magnetic susceptibility as a function of temperature in the range of 4.2–900 K has been evaluated and found to lie in between \(-40\) and \(-38 \text{ cm}^3/\text{mol}.\)\(^{154}\)

The energy–wave-vector relation for holes in III–\(V\) compounds, including GaSb, contains a linear-\(k\) term owing to lack of inversion symmetry in their crystal structure, by the spin-orbit splitting. As shown by Dresselhaus, Kip, and Kittel\(^{159}\) because of the linear-\(k\) term, the light and heavy hole bands are split into two nondegenerate bands, and the energy maxima of the valence bands are not at \((0,0,0)\). The maxima of the heavy hole bands are shifted in [111] direction and that of the light hole bands in [100] direction. From an analysis of transport data the following values for the difference of energies at the top of the bands and at \(k = 0\) have been found.\(^{160,161}\)

\[ \Delta E[111]:20 \text{ meV}; \Delta E[100]:5 \text{ meV}; \]
\[ \Delta E[111] - \Delta E[100]:7.5 \text{ meV}. \]

The influence of the linear-\(k\) term on the shape of the isoenergetic surfaces in \(p\)-GaSb has been deduced by Robert et al.\(^{162}\) from galvanometric measurements. They have shown that the nonquadratic band model employed for Ge and Si is insufficient to account for all the observed galvanometric phenomena. They determined the anisotropy coefficients of the light and heavy hole ellipsoids along the [100] and [111] directions to be 1.66 and 3, respectively.

The valence band parameters \(A, B\) and \(C\) used in the nonquadratic \(E - k\) relation calculated using \(k \cdot p\) theory\(^{163}\)

are 11.7, 8.19 and 11.07, respectively. From cyclotron resonance measurements on \(p\)-GaSb in the range 12–20 K, Stradling\(^{164}\) determined these values to be 11 ± 0.6, 6 ± 1.5 and 11 ± 4, respectively, which are in good agreement with the theoretically predicted values.

### B. Effective masses of electrons and holes

The effective masses of electrons and holes have been evaluated by cyclotron resonance technique and from the density of state analysis of transport data.\(^{165,166}\) In Table IV, the effective masses for electrons \((m_e)\) in the \(\Gamma\), \(L\) and \(X\) conduction bands and that for holes \((m_p)\) in heavy and light hole valence bands are given with the density of state masses.

The density of state effective mass obtained from electron concentration (transport) measurements can be different from that obtained from reflection measurements.\(^{154}\) The difference is due to the anisotropy of the upper subband. High resolution magneto-absorption measurements made at photon energies just above the intrinsic absorption edge in GaSb have revealed an oscillatory spectrum. The value of the energy gap found is \(E_g=0.813 \pm 0.001\) eV and electron effective mass, \(m_e=(0.47 \pm 0.003)m_0.\)\(^{154}\) The optically determined hole mass is considerably smaller than the one derived from electrical measurements.

Due to close proximity of the \(L\) band to the conduction band minimum, appreciable population of electrons exists in the \(L\) band above room temperature. Since the effective mass of electron is more in the \(L\) band, it will affect the electron mobility above room temperature. Moreover, for Schottky diodes the Richardson constant (and hence the barrier height) will also get affected by the population of electrons in the \(L\) band.

### C. Electron transport

The transport properties of GaSb have been the subject of investigation for the last 3 decades.\(^{167–184}\) This is because of some special features of its band structure. Transport in

<table>
<thead>
<tr>
<th>Notation</th>
<th>Numerical value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_e(\Gamma))</td>
<td>0.0412</td>
<td>from cyclotron resonance of hot electrons in the temperature range of 1–30 K</td>
</tr>
<tr>
<td>(m_e(L))</td>
<td>0.0396</td>
<td>same data as above but by taking into account the nonparabolicity and polaron effect</td>
</tr>
<tr>
<td>(m_e(X))</td>
<td>0.11</td>
<td>from transverse conductivity</td>
</tr>
<tr>
<td>(m_e(L))</td>
<td>0.05</td>
<td>from longitudinal conductivity</td>
</tr>
<tr>
<td>(m_p(L))</td>
<td>0.226</td>
<td>density of state mass</td>
</tr>
<tr>
<td>(m_p(X))</td>
<td>0.51</td>
<td>from longitudinal conductivity</td>
</tr>
<tr>
<td>(m_p(h))</td>
<td>0.28</td>
<td>from conductivity data</td>
</tr>
<tr>
<td>(m_p(l))</td>
<td>0.05</td>
<td>from conductivity data</td>
</tr>
<tr>
<td>(m_{de})</td>
<td>0.82</td>
<td>density of state mass</td>
</tr>
</tbody>
</table>

Table IV. Effective masses of electrons and holes (in terms of free electron mass, \(m_0\)) (compiled from Refs. 165 and 166).
n-type GaSb is complicated due to the contributions from Γ, L and X conduction bands. Experimental data on transport coefficients can be consistently explained by a three band model, the X bands contributing to transport above 180 °C. The room temperature electron mobility (in cm²/V s) for a sample with \( n = 1.49 \times 10^{18} \, \text{cm}^{-3} \) was found to be 3750, 482 and 107 at the Γ-, L- and X-band minima, respectively. Furthermore, for the L-band at room temperature, the mobility was found to be 500–800 and 800–1600 cm²/V s at 120 K. Fig. 22 shows the temperature dependence and the contributions of various scattering mechanisms to the electron mobility.

Sagar discussed the results of Hall coefficient measurements on n-type material on the basis of the two-band model. The purer samples have higher Hall coefficient at any given temperature. The special features are the increasing Hall coefficient with increasing temperature for the pure samples and the appearance of a maximum for the heavier-hole band for a sample with \( n = 1.49 \times 10^{18} \, \text{cm}^{-3} \) was found to be 3750, 482 and 107 at the Γ-, L- and X-band minima, respectively. Furthermore, for the L-band at room temperature, the mobility was found to be 500–800 and 800–1600 cm²/V s at 120 K. Fig. 22 shows the temperature dependence and the contributions of various scattering mechanisms to the electron mobility.

Dependence of the Hall coefficient for Se- and Te-doped samples. The difference is most pronounced at heavy doping and disappears for very pure samples. One possible interpretation is that impurity-band conduction is dominating in this region, and that this depends on the nature of the donor. The two subbands of the conduction band of GaSb both contribute strongly to the magnetoresistance. In purer samples, the magnetoresistance decreases with decreasing temperature, whereas in heavily doped samples, the opposite trend is observed. The influence of the second band becomes noticeable as soon as the electron concentration surpasses the value of \( 1.25 \times 10^{18} \, \text{cm}^{-3} \). Pressure dependence of the resistance, Hall coefficient and the thermoelectric power confirmed the presence of three subbands in the conduction band. The third subband appears only at 25 000 kg/cm². From the Z coefficients (piezoresistance) measurements under hydrostatic pressure, the (000) subband has been found to displace upward relative to the (111) subband with increasing pressure. Its contribution to the conductivity therefore decreases. Since the density of state in the (000) band is considerably smaller than in the (111) band, there are only few electrons in the (000) band; however, they contribute considerably to the conductivity because of their high mobility. When these electrons are brought into the (111) band by pressure, their small number does not add much to the contribution of this subband to the conductivity and piezoresistance. From thermoelectric power measurements on p-GaSb in the temperature region from 280 K to 3000 K the effective mass of the holes has been found to strongly depend on temperature and to be doping dependent. An abrupt change of the thermoelectric power is observed at the melting point.

In GaSb, the donor states below the (000) minimum fuse into the conduction band; the ones lying below the (111) minima, however, keep a finite ionization energy because of the larger effective mass of the electrons in these minima. These discrete impurity levels lie a few hundredths of an eV above the energy of the states farthest from the valence band. The bandgap in GaSb is considerably smaller than in the III-V compounds. Since the smaller effective mass of the electrons in these minima.

The pressure variation of the resistivity of S-, Se- and Te-doped GaSb has been studied to 50 kbar. All three types exhibit a saturation in resistivity at the highest pressures attained, although the resistivity of S- and Se-doped samples increases several orders of magnitude before saturation, in contrast to Te-doped samples, whose resistivity increases only by a factor of 14. The saturation in resistivity is due to the X₁₁₁ minima becoming the lowest conduction-band edge at these pressures.

Even though numerous investigators have explained their Hall data on n-GaSb by considering the effects of a relatively low lying L and X conduction bands, there are,
however, some peculiarities in the electrical properties of $n$-GaSb occurring at lower doping levels which do not appear to be the result of multiple-band conduction. For example, the mobility at low temperatures is observed to increase monotonically with increasing electron concentration for Te-doped GaSb.\textsuperscript{169} Also, the diffusion of lithium into Te-doped material has resulted in significant increase in electron mobilities coupled with modest increase in electron concentration.\textsuperscript{170,171} Long and Hager,\textsuperscript{172} in their investigation of near resonance scattering in GaSb at low temperatures, pointed out the basic importance of compensation in regard to the observed increase in mobility with electron concentration. This behaviour is in contrast to that found in $n$-type GaAs and InAs, where compensation is significantly lower.\textsuperscript{173} Later, Baxter and co-workers\textsuperscript{174} illustrated the effect of compensation on Coulomb scattering from the well known Brooks–Herring treatment.\textsuperscript{175} The ionized impurity mobility is in general an increasing function of carrier concentration $n$ and inversely proportional to $N_f$, the ionized impurity concentration. In the absence of compensation, $N_f$ is equal to $n$; however, with high concentration of compensating centres, $N_f$ varies much more slowly with $n$ and the variation of mobility is entirely controlled through $n$. Further, to fit the mobility data for low electron concentrations the required hole concentration is 2–3 times more than that observed in undoped GaSb.\textsuperscript{174} Baxter and co-workers\textsuperscript{174} have explained this with the double ionizable nature of the native defect. The higher hole concentration needed to fit the data arises from a deep lying acceptor level which is not appreciably ionized at room temperature in the undoped samples. Such a level would, of course, be completely ionized in $n$-type material and account for the apparently high estimates for the compensating acceptors. Several workers have adopted the approach of compensating the crystals with Te to shift the Fermi level toward the conduction band and hence observe the deeper level; but, as evidenced from luminescence measurements\textsuperscript{176} and pointed out by Johnson and co-workers,\textsuperscript{177} incorporation of donor dopant Te is accompanied by the formation of an additional acceptor state near the singly ionized state of the native defect, which is often confused with the energy levels of the native acceptor.\textsuperscript{178–182} This would also explain the high estimates for the compensating acceptors. Shubnikov–de Haas oscillations have been observed in Te-doped GaSb diffused with lithium as shown in Fig. 23.\textsuperscript{183} The oscillation has been attributed to electron population in the $L$ band.\textsuperscript{183} Recently, we have studied the hole transport properties of undoped and tellurium compensated $p$-GaSb in the temperature range of 4.2–300 K with an aim to clarify these anomalies, paying special attention to the behaviour of the deeper energy levels. This aspect is discussed below.

D. Hole transport

In $p$-type III–V compounds, the dominant factors limiting mobility have been found to be acoustic, nonpolar and polar optical phonons and ionized impurity scatterings.\textsuperscript{163,184} In $p$-GaSb, owing to the close proximity of the heavy and light hole bands, intervalley and intravalley scatterings occur. Thus, the contributions from both the light hole and heavy hole bands to various transport properties should be taken into account.\textsuperscript{159,160} The hole transport properties at low temperatures can be explained consistently by the multiellipsoidal model to take into account the shift of the heavy and light hole bands away from $k = 0$, whereas at high temperatures a warped sphere model (as in Si and Ge) is adequate.\textsuperscript{159,160} Analyses of transport data between 77 and 300 K have to take into account the intermediate region between the two limiting cases in which the effective mass of heavy holes varies with temperature as shown in Fig. 24.\textsuperscript{185} Fig. 25 shows the temperature dependence of mobility along with the contributions of heavy and light holes without taking into account of the variation of heavy hole effective mass with temperature.\textsuperscript{159}

By taking into account the temperature dependence of heavy hole density of states effective mass, we have investigated the transport properties of undoped and Te compensated $p$-GaSb with the knowledge of defect levels from luminescence studies.\textsuperscript{186} Evidence for self-compensation is seen on Te doping by the formation of an Te-related acceptor complex. Excellent agreement between the theoretically calculated and experimentally measured mobilities has been obtained, by including the Te-related acceptor V$_{Ga}$Ga$_{Sb}$, Te$_{Sb}$ apart from the doubly ionizable native defect V$_{Ga}$Ga$_{Sb}$. The mobility as a function of temperature for undoped samples grown from stoichiometric and nonstoichiometric melts along with Te compensated samples to various degrees are shown in Fig. 26. As depicted in Fig. 26, with increase in Te concentration the mobility decreases and a shift in the mobility peak to higher temperature is observed. The partial mobilities for various scattering mechanisms along with the

![Figure 23](image-url) FIG. 23. (a) Transverse and (b) longitudinal magnetoresistance oscillations at various temperatures for Te-doped $n$-GaSb samples after Li diffusion (from Ref. 183).
total mobility for the undoped and Te compensated samples are shown in Figs. 27 and 28, respectively. At low temperatures, the largest contribution to hole scattering comes from ionized impurities for both the samples. At room temperature nonpolar and polar optical phonons and acoustic scatterings all make significant contributions for the undoped sample, whereas ionized impurity scattering is still dominant for the Te compensated sample.

Johnson et al.\textsuperscript{187} have also studied the effect of compensation in MBE grown $p$-GaSb epilayers by varying the Sb/Ga ratio in the flux. They found that the layers with the lowest residual acceptor concentrations are not those that display the highest hole mobility, confirming the effect of compensation.

Fig. 29 shows the intrinsic carrier concentration as a function of temperature. As can be seen, GaSb achieves an intrinsic carrier concentration of $n_i \approx 10^{17}$ cm$^{-3}$ in the neighborhood of 600 K.\textsuperscript{188} The temperature dependence of mobility above room temperature for a typical sample with $N_A \approx 10^{17}$ cm$^{-3}$ is shown in Fig. 30. At a temperature of approximately 630 K, the sample converts from $p$ to $n$ type due to rapidly increasing intrinsic carrier concentration and the larger mobility of the electrons. The exact temperature at which this conversion takes place depends, among other things, on the acceptor concentration and is lower for lower densities of acceptors.

For GaSb there is no exhaustion region where the electron population of the impurities remains constant while the Fermi level varies with temperature. Hence the employment of data from luminescence experiments is all the more essential to interpret the Hall data accurately and reliably.
E. Magnetophonon effect

Oscillations in the ohmic longitudinal magnetoresistance (OLMR) have been observed in $n$-GaSb with carrier concentration in excess of $10^{17} \text{cm}^{-3}$ in the temperature range of 20–80 K. These oscillations were interpreted as magnetophonon and spin-magnetophonon oscillations. However, for the degenerate case oscillations due to transitions of electrons between the Fermi level and the Landau levels, with absorption or emission of an LO phonon, can occur at quantized magnetic fields.

F. Electron and hole transport in ternaries

The electrical properties of InGaSb have been investigated in detail by Joullie and co-workers. As-grown undoped In$_x$Ga$_{1-x}$Sb is $n$ type in nature above $x=0.5$ and $p$ type for $x$ below 0.5. The compositional dependence of carrier concentration is shown in Fig. 31. The Hall mobility as a function of $x$ is shown in Fig. 32. As can be seen from the figure, the electron mobility steadily decreases from pure InSb value till $x=0.5$ (to the $n-p$ transition), after which the hole mobility falls to pure GaSb value.

In the regime of low $x$ in Al$_x$Ga$_{1-x}$Sb, the material has direct gap with $G$ being the conduction band minimum. For $x>0.52$, the material is indirect with the conduction band minimum at $X$. Donor related deep traps were detected in Te-doped Al$_x$Ga$_{1-x}$Sb for $x>0.2$. The concentration of deep traps increases steeply with $x$ in the range $0.3<x<0.5$ and saturates for $x>0.5$. The deep trap concentration also increases linearly with donor concentration for the same Al composition. In the temperature-dependent Hall effect measurements both shallow donor and deep donor levels were observed. The characteristics of deep traps in Te:AlGaSb are similar to the $DX$ centre in AlGaAs. This implies that the deep traps in Te:AlGaSb arise from the same origin as the $DX$ centre in AlGaAs. The shallow donor predominates for $x \leq 0.3$, while the deep donor predominates for $x \geq 0.4$ in concentration. Considering the energy separation between the $\Gamma$ and $L$ band, and the effective mass in $L$ band, the deep electron traps should be detected even in GaSb if the $DX$ centre is simply a donor associated with the $L$ band. $DX$ centres are observed in S:GaSb, but not in Te- and Se-doped ones as is discussed later in Sec. VII. The deep traps in
Te:AlGaSb cannot be explained by the band crossing of \( \Gamma \) and \( L \) bands, since electron traps were not detected at \( x = 0.2 \) where the \( \Gamma \) and \( L \) bands cross. The sulfur related shallow states in GaSb are linked to the \( \Gamma \) minimum. The deep donors in S:GaSb have two states which exhibit large lattice relaxation.

The compositional dependence of the direct energy gap in \( \text{Ga}_{x}\text{In}_{1-x}\text{Sb} \) at 300 K is given by:\(^5\)

\[
E_g = 0.172 + 0.165x + 0.413x^2.
\]

For the \( \text{Al}_x\text{Ga}_{1-x}\text{Sb} \), the compositional dependences of direct and indirect energy gaps are given below:\(^5\)

\[
E_g = 0.73 + 1.10x + 0.47x^2 \quad \text{(direct gap)},
\]
\[
E_x = 1.05 + 0.56x \quad \text{(indirect gap)}.
\]

VI. OPTICAL PROPERTIES

A. Dielectric constant

The dielectric constants \( \varepsilon(0) \) and \( \varepsilon(\infty) \) were found to be 15.69 and 14.44, respectively, at 300 K using reflectance technique and oscillator fit.\(^{189}\) The real and imaginary parts of the dielectric constant measured by ellipsometric technique are shown in Fig. 33. The values for refractive index \( n \), extinction coefficient \( k \), and reflectance \( R \) calculated from these data are given in Table V for various wavelengths. The temperature dependence of refractive index for undoped GaSb with hole concentration of \( 10^{17} \text{ cm}^{-3} \) is given by:\(^{190}\)

\[
\left( \frac{1}{n} \right) \frac{dn}{dT} = (8.2 \pm 0.2) \times 10^{-5} \text{ oC}^{-1}.
\]

B. Photoconduction

Very little work has been carried out on photoeffects in this material. Spectral sensitivity measurements of photoconductivity were carried out on one \( p \)-type specimen by Frederikse and Blunt.\(^{191}\) Their results indicate energy gaps of 0.65 eV at room temperature and 0.77 eV at 85 K. Habegger and Fan\(^{192}\) have reported observations of long wavelength photoresponse due to impurities. They concluded that there are levels situated at 34, 62, 76 and 103 meV above the...
valence band edge. Lukes\textsuperscript{193} found that the spectral response fell rapidly as the wavelength was decreased, presumably due to high surface recombination. It is estimated from the ratio of photoconductivity (PC) to photoelectrically generated photocurrents that the lifetime is 1 ps.\textsuperscript{194}

C. Photoelectric threshold and work function

Data available in the literature concerning work function and photoelectric properties are meagre.\textsuperscript{195} The values of band gap $E_g$, work function $\phi$, photoelectric threshold $\Phi_i$, direct transition threshold $\Phi_d$ and electron affinity $\chi$ are given below for $p$-GaSb (110) with $N_A = 1.2 \times 10^{17}$ cm$^{-3}$ and resistivity of 0.07 Ω cm.

\begin{equation}
E_g = 0.70 \text{ eV}, \quad \phi = 4.76 \text{ eV}, \quad \Phi_i = 4.76 \text{ eV},
\end{equation}

\begin{equation}
\Phi_d = 5.24 \text{ eV}, \quad \chi = 4.06.
\end{equation}

D. Nonlinear optical effect

The unique contribution of III–V compounds to nonlinear optics has been in the observation of reflected harmonics. This is mainly because many of the III–V compounds are opaque to the second harmonic of ruby laser light and thus experimentally there is no confusion between a weak reflected harmonic and scattered radiation from a much stronger transmitted harmonic. Bloembergen et al.\textsuperscript{196} calculated the relative value of $\chi_3$ of GaSb with respect to KDP. For $\lambda = 1.06 \mu$m, $\chi_3$ of GaSb is 1300 times that of KDP ($=6 \times 10^{-9}$ esu) and at $\lambda = 0.0694 \mu$m, it is 400 times larger.

E. Radiative recombination and stimulated emission

Johnson and co-workers\textsuperscript{177} have studied absorption, PL and injection luminescence as a function of temperature. The band–band peak increases with the free hole concentration. In $p$-type samples, compensated with Se or Te, several new bands appear, some of which are characteristic of pure Se or Te. At high donor doping levels the band–band peak shifts to higher energies due to the Burstein–Moss effect.\textsuperscript{197}

In alloyed diodes prepared on $p$-type crystals, Calawa\textsuperscript{198} has observed a deep level band at 77 K which neither shifts with current nor with magnetic field, clearly indicating that it is not a band–band transition. The peak intensity increases linearly with current, becoming sublinear at high current densities. The external quantum efficiency is 8.5% at 77 K. A new deep level is seen in junction regrowth layers containing tin. Diodes fabricated by diffusion of zinc into moderately heavily doped $n$-GaSb show a broad band around 720 meV at 77 K. This band shifts to higher energy and narrows as the current increases and at high currents a new peak appears at 790 meV. The shifting peak was attributed to a transition from an acceptor impurity band to a donor level on the $n$ side of the junction and the high current peak to a valence band donor level transition. Peaks shifts with current were also observed in heavily doped Cd:Te grown junctions that apparently lased at higher currents. The low density of states in the conduction band and the close proximity of the next higher lying minima, which can become populated at high carrier concentrations, or at high injection levels can lead to profound changes in the recombination statistics as the Fermi level rises.

Increase in transmissivity and extension of infrared spectrum of undoped $p$-GaSb by lithium diffusion has been carried out by Hrostowski and Fuller.\textsuperscript{199} The room temperature absorption spectra of GaSb before and after compensation by Li diffusion are shown in Fig. 34. The increase in transmissivity is attributed to reduction in free carrier absorption.

Lasing has been achieved in GaSb at 77 K by injection and by electron bombardment.\textsuperscript{200} The complete details of the structures, doping levels, lasing threshold and operation conditions are given in the respective reports (see Refs. in Ref. 200).

VII. DEFECTS AND IMPURITIES

A. Extended defects

Several studies have been carried out to investigate the defects generated during the growth of bulk GaSb crystals.\textsuperscript{35,201–207} Influence of crystallographic orientation of the seed on the formation of dislocations and twins in single crystals (grown with encapsulant) has been studied for $\langle 111 \rangle$, $\langle 112 \rangle$ and $\langle 115 \rangle$ orientations.\textsuperscript{201} It has been found that the orientation $\langle 115 \rangle$ is the most favourable one for lowering the dislocation density and for depressing twin formation. Also the twin formation is greatly influenced by the polarity of the $\langle 111 \rangle$ seed.\textsuperscript{203} In the case of a seed with $\langle 111 \rangle$B plane oriented into the melt, twin-free GaSb single crystals can be obtained; however, with the opposite orientation (Ga plane) of seed, twinning always occurred. The influence of different orientations of the seed on crystal growth and twinning for the case of the Czochralski method...
in a hydrogen atmosphere has also been investigated\(^{207}\) and it is concluded that the tendency to polycrystalline growth and twinning increases in the following order: \(\langle 111 \rangle\), \(\langle 112 \rangle\), and \(\langle 100 \rangle\). Characterization of extended defects in heavily Te-doped \(\langle 111 \rangle\) CZ-grown GaSb single crystals has been carried out by Doerschel and Geissler.\(^{204}\) The nature and density of the defects are correlated with the local tellurium concentration. Prismatic dislocation loops with \(\langle 110 \rangle\) and \(\langle 111 \rangle\) habit planes (perfect or faulted loops) are the dominant defects. Extended dislocation clusters consisting of complete dislocations with a Burgers vector of the type \((a/2)(\overline{1}10)\) have also been observed. Since the dislocations do not lie in \(\langle 111 \rangle\) glide planes they move by climb, especially in \(\langle 110 \rangle\) planes. Often, large multi-layered planar defects with displacement fringe contrast are also observable near dislocation clusters. They have been identified as Ga\(_2\)Te\(_3\) precipitates lying in \(\langle 111 \rangle\) lattice planes. The prismatic dislocation loops are generated at a tellurium concentration of \(3 \times 10^{18} \text{ cm}^{-3}\) and the dislocation clusters and large planar defects occur at a tellurium concentration of about \(10^{19} \text{ cm}^{-3}\).

**B. Native defects**

Undoped, pure GaSb is usually \(p\) type in nature with acceptor concentration of \(~10^{17} \text{ cm}^{-3}\)^{208} Because of its small band gap, GaSb begins to show complications due to intrinsic conduction at relatively low temperatures. By the year 1963, there was fairly convincing evidence that the troublesome background acceptors were related to native defects rather than chemical impurities. Experiments involving ion pairing between Li and the unknown acceptor showed the acceptor to be doubly ionizable chemical defect that could have escaped detection by mass-spectrographic analysis.\(^{17}\) The residual acceptors can be made electrically ineffective by ion-pairing with lithium. According to Baxter and co-workers,\(^{17}\) the hole density decreases from \(10^{17}\) to \((2\sim3) \times 10^{15} \text{ cm}^{-3}\) when lithium is diffused into GaSb. Subsequently, Reid and co-workers\(^{18}\) performed a series of experiments in which GaSb crystals were grown from nonstoichiometric melts. As the Sb concentration in the melt is increased above 60%, one obtains significant reductions in the level of background acceptors, indicating that the acceptor defect involves either excess of Ga or a deficiency of Sb in the crystal. They suggested that the most likely candidate was a Ga on a Sb site. The model of a \(V_{Ga}Ga_{Sb}\) complex as the dominant acceptor is in agreement with the results of thermodynamical investigations;\(^{209}\) however, Zeeman experiments show that the defect has tetrahedral local symmetry and thus it seems difficult to reconcile these conclusions.\(^{210}\) Both singly and doubly ionizable acceptor models have been proposed to account for the behaviour of this defect in relation to the electrical and optical properties of GaSb.

The results of theoretical calculations which give the concentration of each of the native defects like \(V_{Ga}\), \(V_{Sb}\), \(Ga_{Sb}\) and \(Sb_{Ga}\) for crystals grown from Ga and Sb melts as a function of temperature are shown in Figs. 35 and 36. As can be seen from the figure, with decrease in growth temperature the native acceptor concentration decreases.

![FIG. 35. Temperature dependence of vacancy concentration in GaSb (from Ref. 209).](image)

The low temperature photoluminescence (PL) spectrum of undoped GaSb exhibits about 20 transitions in the energy interval of 680–810 meV, but only a part of these transitions has been associated with specific impurities or defects, and these are listed in Table VI.\(^{211\sim213}\) The dominant transition is at 777 meV. In S:GaSb, the 777 meV is shifted by 4–6 meV to lower energy and the S-related peak appears in the range of 731–733 meV. The S donor level is at 81 meV below the conduction band. The Te- and Zn-related peaks appear at 740 and 775 meV, respectively.

Typical PL spectra at 4.2 K for GaSb grown by LPE at various temperatures from Ga- and Sb-rich melts are shown in Fig. 37. The highest purity samples which exhibit high luminescence efficiency are the LPE-grown ones.\(^{95}\) Moreover, for MBE-grown GaSb layers on GaAs, the PL peak positions are slightly different than usually seen in bulk. This has been attributed to strain present in the epilayer.\(^{211}\)

Efforts have been made by several workers in the past as well by our group to reduce the native defect concentration during growth from nonstoichiometric melts,\(^{18,214}\) and by postgrowth annealing experiments.\(^{214}\) Postgrowth annealings in Sb- and Ga-rich atmospheres do not effectively decrease the native defect concentration. On the other hand, crystal growth from Ga- or Sb-rich melts results in decrease in native defect concentration up to two orders of magnitude with increased mobility.\(^{18,214}\) However, the higher mobility values observed in these crystals should be treated with caution. Anomalously high hole mobility in GaSb has been attributed to sample inhomogeneity.\(^{215}\) Our recent investigation on compositional analysis of as-grown GaSb from nonstoichiometric melts shows the presence of metallic inclusions (Ga
and Sb) which would show high mobility in the crystals. Thus while concluding about the high crystalline quality through carrier mobility, one should rule out the possibility of metallic inclusions. These metallic inclusions would limit the usage of wafers prepared from GaSb ingots grown from nonstoichiometric melts for device fabrication. Thus the option of reducing native defect concentration by nonstoichiometric melt growth does not seem advantageous for obtaining high quality wafers with uniform properties.

Theoretical calculations for the electronic structure of the divacancies at different charge states in GaSb based on self-consistent tight-binding theory has been carried out by Xu.\textsuperscript{216} The energy positions and localizations of the defect levels have been calculated for the predicted charge states. Each divacancy at a charge state introduces seven defect levels, three at the edges of the lower gap and four in or around the fundamental band gap.

### C. Shallow dopant impurities

To grow n or p-type GaSb various dopants have been used.\textsuperscript{217–219} Usually, Te, Se and S are used to grow n-GaSb and Zn, Ge and Si for p-GaSb. The binding energies of various impurity levels in GaSb are shown in Fig. 38.\textsuperscript{220–227} The donor states of tellurium in GaSb can be described satisfactorily by the hydrogenic model.\textsuperscript{224} The binding energies calculated in accordance with this model are in agreement with the experimental values. The energy positions of selenium and sulfur impurity levels in GaSb are affected by the deviation from the hydrogenic model along the Te \( \rightarrow \) Se \( \rightarrow \) S series and by the corresponding increase in the binding energy.\textsuperscript{228–231} As clearly shown in the figure, Ge, Li, Si, Ga, Zn, Sb and Cu are shallow acceptors and S, Te and Se are shallow donors in GaSb. However, it should be noted that Fe is a deep acceptor. With carrier concentration of the order of \( 10^{17} \text{ cm}^{-3} \), the highest resistivity is obtained by Cu (0.8 \( \Omega \) cm).\textsuperscript{217} Mn doping also gives rise to p-type conductivity.

The solubilities of Se and Te at the melting point are \( 1.5 \times 10^{18} \text{ cm}^{-3} \). Above these concentrations, compounds form between Se or Te and Ga.\textsuperscript{154} Investigation of impurity variations by cathodoluminescence (CL) imaging in GaSb:Te has been carried out by Chin and Bonner.\textsuperscript{231} Within the resolution of the CL technique, no evidence of a second phase is found in GaSb crystals doped with Te to the solubility limit.

The formation of p-GaSb by Ge doping is surprising. In view of the atomic covalent radius, it is expected that Ge would substitute Ga making GaSb n-type (radii: Ga, 1.25 Å; Sb, 1.41 Å; Ge, 1.22 Å). Even the electronegativities of Ge (2.0), Sb (1.8) and Ga (1.8) would not suggest the substitution of Ge in Sb site. Sulfur doping seems to be most difficult due to its high evaporation rate. The most suitable way of S doping is done by using Sb\(_2\)S\(_3\) in a flowing atmosphere of hydrogen and sulfur vapour.\textsuperscript{232} Following the idea of lattice hardening by isoelectronic dopants as observed in other

<table>
<thead>
<tr>
<th>Energy (meV)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>830</td>
<td>((e,h)) recombination (77 K)</td>
</tr>
<tr>
<td>812</td>
<td>band gap</td>
</tr>
<tr>
<td>810</td>
<td>free exciton</td>
</tr>
<tr>
<td>808</td>
<td>excitonic transition</td>
</tr>
<tr>
<td>807</td>
<td>excitonic transition</td>
</tr>
<tr>
<td>805</td>
<td>exciton bound to ((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>803</td>
<td>Exciton bound to ((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>801</td>
<td>D(^+)-Si-acceptor</td>
</tr>
<tr>
<td>800</td>
<td>Exciton bound to ((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>797</td>
<td>Exciton transition</td>
</tr>
<tr>
<td>796</td>
<td>Exciton bound to ((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>795</td>
<td>Exciton transition</td>
</tr>
<tr>
<td>792</td>
<td>Exciton bound to ((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>781</td>
<td>C-(((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>777</td>
<td>D(^+)-(((V_{Ga,Ga,Sb})^0)</td>
</tr>
<tr>
<td>775</td>
<td>C-Zn acceptor</td>
</tr>
<tr>
<td>765</td>
<td>LO phonon replica of the 796 meV transition</td>
</tr>
<tr>
<td>758</td>
<td>Acceptor B</td>
</tr>
<tr>
<td>746</td>
<td>LO phonon replica of 777 meV</td>
</tr>
<tr>
<td>740</td>
<td>C-((V_{Ga,Ge,Sb}Te,Sb)^0)</td>
</tr>
<tr>
<td>728</td>
<td>LO phonon replica of 758 meV</td>
</tr>
<tr>
<td>717</td>
<td>Exciton bound to ((V_{Ga,Ge,Sb})^-)</td>
</tr>
<tr>
<td>710</td>
<td>C-((V_{Ga,Ge,Sb})^-)</td>
</tr>
<tr>
<td>682</td>
<td>LO phonon replica of 710 meV transition</td>
</tr>
</tbody>
</table>

$\text{FIG. 36. Temperature dependence of antisite concentration in GaSb (from Ref. 209).}$

$\text{TABLE VI. PL transitions observed in bulk GaSb at 4.2 K (compiled from Refs. 211–213).}$
grow from Sb melts. The growth temperatures by DLTS and thermally stimulated capacitance spectroscopy. Deep level impurities have been carried out using elemental indium and GaN. How-ever, lattice hardening did not occur and the dislocation density remained same as in the case of the undoped crystals. The segregation coefficients of various impurities in GaSb are listed in Table VII.154

III–V compounds, indium and nitrogen doping of GaSb has been carried out using elemental indium and GaN.233 However, lattice hardening did not occur and the dislocation density remained same as in the case of the undoped crystals. The segregation coefficients of various impurities in GaSb are listed in Table VII.154

D. Deep level impurities

The shallow donors Te, Se and S also revealed deep impurity levels in the band-gap intrinsic of the dopant species. The deep level properties of Te, Se and S doped GaSb on MBE-grown epilayers115 have been evaluated by deep level transient spectroscopy (DLTS) and in bulk crystals234 by DLTS and thermally stimulated capacitance spectroscopy (TSCAP). The trap levels reveal various concentrations and activation energies. These are listed in Table VIII. The trap densities in Te- and Se-doped samples are two orders of magnitude lower than the shallow donor concentration. Interestingly, the DLTS spectrum of S:GaSb exhibits DX-like nature with trap concentration comparable to that of shallow donor concentration. These electron levels are commonly detected in n-GaSb, but not in undoped p-GaSb, suggesting that the level is not a simple native defect, but may be connected with the impurity used for n doping; however, the exact origin of this level is not clear and is subject of further investigation. Poole et al.115 proposed for S:GaSb a coordinate model for a large lattice relaxation of sulfur donor. They115 attributed the difference in deep level properties of various donors to residual sulfur contamination in the MBE-grown layers. However, the difference in deep level properties of the bulk samples also indicates that it is dopant intrinsic.234 By numerically deconvoluting the DLTS spectrum of S:GaSb, we have observed two peaks with different activation energies.234 Such a splitting has been found previously in a Si-related DX centre in GaAs under hydrostatic pressure (30 kbar).235 It is obvious that the splitting in GaSb cannot be due to alloy broadening as strongly argued by Mooney, Caswel, and Wright to explain the multiple peaked DLTS spectra due to a DX centre in AlGaAs.236 Our TSCAP measurements also showed large nonexponential capacitance transient with multiple peak nature of S:GaSb in agreement with the DLTS measurements.234 Since GaSb doped with sulfur shows DX centres even at atmospheric pressure and under nondegenerate doping conditions, it is most suitable for fundamental investigation of this metastable level thus avoiding alloy broadening effects. Very recently, Hubk

![FIG. 37. Typical PL spectra of undoped p-GaSb at 4.2 K for (a) bulk substrate, (b)–(e) LPE-grown epilayers from Ga melts, (f) epilayers grown from Sb melts. The growth temperatures (in °C) are (b) 580, (c) 550, (d) 500, (e) 450, (f) 600 and (g) 630 (from Ref. 95).](image)

![FIG. 38. Impurity levels (in meV) of GaSb (from Ref. 220).](image)

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.3</td>
</tr>
<tr>
<td>Cd</td>
<td>0.02</td>
</tr>
<tr>
<td>In</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
</tr>
<tr>
<td>Ge</td>
<td>0.32</td>
</tr>
<tr>
<td>Sn</td>
<td>0.01</td>
</tr>
<tr>
<td>As</td>
<td>2–4</td>
</tr>
<tr>
<td>S</td>
<td>0.06</td>
</tr>
<tr>
<td>Se</td>
<td>0.4</td>
</tr>
<tr>
<td>Te</td>
<td>0.4</td>
</tr>
</tbody>
</table>

![TABLE VII. Distribution coefficients ($C_i/C_i$) of dopants in GaSb (from Ref. 154).](table)

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_s$ (meV)</th>
<th>$E_c$ (meV)</th>
<th>$\sigma$ (cm$^2$)</th>
<th>$N_T/N_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>280 (287)</td>
<td>200 (220)</td>
<td>$6 \times 10^{-18}$ ($7 \times 10^{-19}$)</td>
<td>1 (1)</td>
</tr>
<tr>
<td>Se</td>
<td>315 (320)</td>
<td>195 (180)</td>
<td>$2 \times 10^{-20}$ ($9 \times 10^{-21}$)</td>
<td>0.045 (0.030)</td>
</tr>
<tr>
<td>Te</td>
<td>310 (312)</td>
<td>190 (174)</td>
<td>$3 \times 10^{-20}$ ($2 \times 10^{-20}$)</td>
<td>0.015 (0.010)</td>
</tr>
</tbody>
</table>

![TABLE VIII. Electrical properties of deep levels in Te-, Se- and S-doped GaSb (from Refs. 115 and 234). Here $E_s$, $E_c$, $\sigma$, $N_T$ and $N_D$ are the mean emission energy, mean capture energy, capture cross-section, total deep trap density and total donor concentration respectively. The bracketed values are for the vertical Bridgman grown bulk GaSb and the unbracketed ones for the MBE grown GaSb layers.](table)
et al.\textsuperscript{237,238} have also inferred the $DX$-like nature of the S donor in GaSb using Hall, photo-Hall and persistent photoconductivity measurements.

The $DX$-like centre dominates in Hall measurements between 77 and 300 K. However, if a deep level is the main source of free carriers in a wide temperature range, the evaluation of capacitance in DLTS studies of such a level becomes complicated due to transient nonexponentiality. This nonexponentiality can be avoided if samples are measured where the concentration of shallow impurities is high in comparison with that of deep levels (10 times or more). Since the $DX$ centre is difficult to observe in $p$-type material, it is necessary to prepare $n$-GaSb crystals doped both with sulfur and with some shallow donor impurity like tellurium.

The donor states in $S$:GaSb tied to various conduction band minima and slow relaxation of electrical conductivity in these samples below 120 K have been studied by Vul \textit{et al.}\textsuperscript{224,228} Low-temperature conductivity exhibits the light-induced Mott transition, indicating the existence of sulfur-related shallow states linked to the $\Gamma$ minimum. On this basis a phenomenological model of the deep donors in GaSb:$S$ is proposed, invoking the existence of two sulfur-related deep states with different photosensitivity and thermally activated capture cross section. Both deep states seem to exhibit large lattice relaxation.

DLTS measurements made on $p-n^+$ junctions of GaSb reveal the presence of a hole trap with activation energy of 0.33 eV, concentration of $5 \times 10^{14}$ cm$^{-3}$ and capture cross section of $1.3 \times 10^{-15}$ cm$^2$.\textsuperscript{229} Kuramochi \textit{et al.}\textsuperscript{240} have also observed deep levels in undoped GaSb grown by MBE. Three hole traps were detected in undoped GaSb whose characteristics are shown in the Table IX. The shallowest level (A) shows low uniform concentration of $10^{14}$ cm$^{-3}$ and is considered to originate from a native defect like $V_{Ga-GaSb}$. The concentration of the trap C decreased from $10^{15}$ to $10^{14}$ cm$^{-3}$ away from the $p-n^+$ interface and is believed to be connected with the diffusion of Te from the $n^+$ substrate to the undoped layer during growth. The trap B gives very weak signal and is similar to that reported by Polyakov \textit{et al.}\textsuperscript{239}

<table>
<thead>
<tr>
<th>Trap</th>
<th>$E_a$ (eV)</th>
<th>$c_p$ (x $10^4$ s$^{-1}$)</th>
<th>$\sigma$ (x $10^{-20}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.25</td>
<td>1.8 (150 K)</td>
<td>23 (150 K)</td>
</tr>
<tr>
<td>B</td>
<td>0.3–0.35</td>
<td>undefined</td>
<td>undefined</td>
</tr>
<tr>
<td>C</td>
<td>0.63</td>
<td>1.0 (292 K)</td>
<td>7.1 (292 K)</td>
</tr>
</tbody>
</table>

E. Magnetic impurities

Recently, there has been some interest in the properties of magnetic impurity centres in GaSb.\textsuperscript{241–243} Mn, Fe and Gd doped GaSb crystals have been investigated. PL and electron spin resonance (ESR) spectroscopic studies indicate the formation of a centre ($V_{Sb} + Mn$, $3d^5 + h$) in Mn:GaSb.\textsuperscript{241} Mn:GaSb exhibits a negative magnetoresistance. The magnitude of the magnetoresistance increases with increase in Mn concentration. This effect was attributed to the spin scattering of holes by the magnetic moments of the manganese ions. On the other hand, the existence of the polarization magnetic moment of the Fe and Gd ions in the GaSb matrix did not give rise to a negative magnetoresistance in Fe:GaSb and Gd:GaSb.

F. Isotopic effects

The values of line widths ($\delta H$ in gauss) and second moments ($\Delta H^2$ in gauss$^2$) for various isotopic composition of GaSb have been studied by the nuclear magnetic resonance (NMR) technique and are listed below.\textsuperscript{244}

- Ga$^{69}$Sb: 5.1 G and 6.5 G$^2$,
- Ga$^{71}$Sb: 5.6 G and 6.2 G$^2$,
- GaSb$^{121}$: 4.7 G and 6.7 G$^2$,
- GaSb$^{123}$: 5.1 G and 8.4 G$^2$.

The antishielding factors for charged impurities arising due to the distortion of the core electrons were evaluated by Oliver\textsuperscript{245} and are 175, 321 and 49 for Ga$^{69}$Sb, Ga$^{71}$Sb and GaSb$^{121}$, respectively.

The experimental values of quadrupole transition probabilities are 12 and 1.55 s for Ga$^{71}$Sb and GaSb$^{123}$, respectively.

G. Self- and impurity diffusion

The self-diffusion and the impurity diffusion coefficients in GaSb have been evaluated using radiotracer, SIMS and $p-n$ junction depth measurement techniques.\textsuperscript{246–251} The results are summarized in Table X. The diffusion of indium during growth depends on the composition of the crystal.\textsuperscript{154} Indium diffuses faster in Sb- than Ga-rich crystals. The diffusion of tin into crystal depends on the carrier concentration. The isochronon diffusion coefficient of zinc at 560 °C is $D = 1.8 \times 10^{-11}$ cm$^2$ s$^{-1}$. A strong dependence of the Zn distribution coefficient on the Zn concentration in the melt in GaSb is observed. With increasing Zn concentration (as well as with increasing Ga content), $K_{Zn}$ decreases. The Li diffusion at 665 °C varies from $10^{-11}$ to $2 \times 10^{-6}$ cm$^2$/s at $10^{16}$ and $7 \times 10^{17}$ cm$^{-3}$, respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$ (cm$^2$ s$^{-1}$)</th>
<th>$Q$ (eV)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>3.2 x 10$^3$</td>
<td>3.15</td>
<td>650–700</td>
</tr>
<tr>
<td>Sb</td>
<td>3.4 x 10$^4$</td>
<td>3.45</td>
<td>650–700</td>
</tr>
<tr>
<td>Mn</td>
<td>8.7 x 10$^{-3}$</td>
<td>1.13</td>
<td>470–570</td>
</tr>
<tr>
<td>In</td>
<td>1.2 x 10$^{-7}$</td>
<td>0.53</td>
<td>400–650</td>
</tr>
<tr>
<td>Sn</td>
<td>2.4 x 10$^{-3}$</td>
<td>0.80</td>
<td>320–570</td>
</tr>
<tr>
<td>Te</td>
<td>3.8 x 10$^{-4}$</td>
<td>1.20</td>
<td>400–650</td>
</tr>
<tr>
<td>Cd</td>
<td>1.5 x 10$^{-6}$</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>4.0 x 10$^{-2}$</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>
H. Ion bombardment induced defects

Optical and electrical studies were made on n- and p-type gallium antimonide irradiated with 4.5 MeV electrons.252 Hall-effect measurements showed that acceptors were produced in the n-type samples and that donors as well as acceptors were produced in the p-type samples. Infrared absorption and photoconductivity studies gave evidence for four defect levels: \( E_v + 0.075 \, \text{eV} \), \( E_v + 0.48 \, \text{eV} \), \( E_v - 0.12 - 0.20 \, \text{eV} \), and \( E_v - 0.47 - 0.50 \, \text{eV} \). The absorption associated with the level \( E_v + 0.075 \, \text{eV} \) is similar to that observed in donor-compensated GaSb. The level \( E_v - 0.47 - 0.50 \, \text{eV} \) is an acceptor level, while the level \( E_v - 0.12 - 0.20 \, \text{eV} \) is probably a donor level. A decrease in conductivity under bombardment by neutrons was found in GaSb.

VIII. SURFACE AND BULK DEFECT PASSIVATION

Defect passivation is interesting both for understanding the physics of the material as well as from the point of view of technological applications. Development of GaSb based devices has been hindered due to high leakage surface currents and fast degradation of the bare surface exposed to ambient. This is due to high surface density and Fermi level pinning, and residual native oxide layer on the surface. This makes surface passivation an essential step in GaSb device technology. Usually, chemical treatment with compounds like \( \text{NH}_4\text{S} \) and \( \text{RuCl}_3 \) results in surface reconstruction due to which the surface recombination rate decreases.253–256 On the other hand, defects in the bulk due to which the surface recombination rate increases.239,253–256 Usually, oxides grown on passivated surfaces exhibit higher resistivity and higher breakdown voltage.255 There has been no specific measurement carried out to determine the surface recombination velocity in GaSb. Nevertheless, the surface recombination velocity can be estimated by using the well known equation

\[
S_p = \sigma_p v_n N_a,
\]

where \( N_a \) is the surface state density, \( v_n \) is the carrier thermal velocity and \( \sigma \) is the recombination cross section. Assuming the values of \( v_n \) and \( \sigma \) to be \( 10^7 \, \text{cm/s} \) and \( 10^{-15} \, \text{cm}^2 \), and substituting the values of \( N_a \) as \( 8 \times 10^{12} \) and \( 5 \times 10^{10} \, \text{cm}^{-2} \, \text{eV}^{-1} \) for unpassivated and sulfur passivated samples,254 the calculated \( S_p \) are \( 5 \times 10^2 \) and \( 8 \times 10^4 \, \text{cm/s} \) for the passivated and unpassivated surfaces, respectively. These are comparable to the \( S_p \) in InP, but lower than in GaAs.

The \( C-V \) characteristics of a typical Al/oxide/n-GaSb MOS at 1 MHz fabricated on untreated and \( \text{RuCl}_3 \) treated GaSb are shown in Fig. 40. The decrease in loop width after passivation also confirms the reduction in the interface state density at the oxide–semiconductor junction. The surface trap densities were found to be of the order of \( 10^{10} \) and \( 10^{12} \, \text{cm}^{-2} \, \text{eV}^{-1} \) for the treated and the untreated samples, respectively. Usually, oxides grown on passivated surfaces exhibit higher resistivity and higher breakdown voltage.255

The effect of passivation on the forward \( I-V \) characteristics of \( \text{Au/n-GaSb} \) Schottky diode fabricated on unpassivated and Ru passivated samples is demonstrated in Fig. 41. For the unpassivated sample (curve 1), two distinct exponential regions with \( n = 1.8 \) and 1.3 at low and high bias respectively can be seen. The passivated diodes exhibit \( I-V \) characteristics with no surface recombination component (\( n \) close to 1) as shown in the figure by curve 2. Also due to reduction in surface channel conductivity, the reverse leak-
Current in diodes decreased by 30–40 times. The improved surface property after passivation is due to the adsorption of the Ru$^{3+}$ ions followed by the partial removal of the surface states from the band gap due to the electrostatic interaction. Similar effects have been observed by Parkinson, Heller, and Miller in GaAs.\textsuperscript{264} The fact that the PL intensities increase with surface treatment for both the $n$- and $p$-type samples indicates that the surface Fermi level is unpinned and there is an increase in band bending. This shows the amphoteric nature of Ru on GaSb surfaces depending on the conductivity type, i.e., positively charged on $p$-GaSb and negatively charged on $n$-GaSb. However, the fact that surface pinning is observed after Schottky barrier formation is due to the reaction of the metals with GaSb which causes repinning. Apart from surface passivation, Ru treatment has also shown increase in room temperature mobility in GaSb polycrystalline samples as a result of grain boundary passivation.\textsuperscript{255}

The surface instability mechanism in GaSb has been discussed by Schirm et al.\textsuperscript{265} Low temperature processes can produce on GaSb a nonequilibrium Ga$_2$O$_3$–Sb$_2$O$_3$ surface oxide layer as follows:

$$2\text{GaSb} + 3\text{O}_2 \rightarrow \text{Ga}_2\text{O}_3 + \text{Sb}_2\text{O}_3.$$  

The only stable phases that can exist in thermodynamic equilibrium with GaSb are Ga$_2$O$_3$ and elemental antimony. Any Sb$_2$O$_3$ should react with GaSb to give rise to Ga$_2$O$_3$ plus free Sb as:

$$2\text{GaSb} + \text{Sb}_2\text{O}_3 \rightarrow \text{Ga}_2\text{O}_3 + 4\text{Sb}.$$  

This reaction spontaneously occurs ($\Delta G = -12$ kCal/mol) even at room temperature. Thus a GaSb surface exposed to air will form a native oxide layer consisting of Sb$_2$O$_3$, Ga$_2$O$_3$ and a fraction of a monolayer of free Sb. This fractional Sb monolayer is quite sufficient to drastically increase the surface recombination velocity and surface leakage.\textsuperscript{261} Similar surface degradation mechanism is well known in GaAs. Alkaline sulphides remove native oxide layer from the surface of GaSb and stabilize it by the formation of stable binary compounds of Ga–S and Sb–S. Perotin et al.\textsuperscript{256} carried out physicochemical analysis of sulfurized GaSb surfaces through ellipsometric, PL and Auger electron spectroscopy measurements. They conclude that a deoxidation plus a sulfurization process leads to a surface of better quality giving good rectifying Schottky diodes. Polluting oxygen and carbon agents are found to be removed from the surface using this process. In addition, the sulfur treatment is shown to stabilize the cleaned surface. These and our studies clearly show that the passivated surfaces are chemically and thermally robust, stable against atmospheric exposure and do not hinder the long term device characteristics.

B. Hydrogen plasma passivation

Even though passivation of bulk defects by hydrogen is now well established, avoiding surface degradation during plasma exposure is not very trivial. In our studies, the existence of defects near the surface has been deduced from the abnormal behaviour of $C$–$V$ characteristics.\textsuperscript{262} During the $C$–$V$ measurements, capacitance transient was observed which indicated slow emission rate of carriers from the defects as shown in Fig. 42. A typical defect layer thickness has been found to range from a few angstroms to a fraction of a micron. The trap densities are comparable in magnitude to the carrier concentration. The defects introduce multiple energy levels in the band gap. This defect layer could be removed in a controlled manner by a slow etchant HCl:H$_2$O$_2$:NaK-tartrate (8:1:1).\textsuperscript{262,266,267}

The effect of atomic hydrogen treatment in a microwave plasma crossed beam and in a direct plasma on the surface properties of GaSb and InGaAsSb has been investigated by...
Polyakov et al.\textsuperscript{260} Both the crossed beam and direct H-plasma exposures led to surface degradation. However, if the H-plasma exposure is followed by a N\textsubscript{2} plasma exposure at 450 °C, the diode leakage currents decreased and the luminescence intensity improved by more than an order of magnitude. Formation of a passivating wide band-gap GaN layer at the surface of GaSb depleted of Sb (Ga-rich layer) by preliminary intense H\textsubscript{2} treatment is thought to be responsible for the effect. Both processes, the Sb depletion and the GaN formation, seem to be temperature activated, since neither treatment in H\textsubscript{2} plasma at 250 °C and subsequent N\textsubscript{2} plasma treatment at 450 °C nor H\textsubscript{2} treatment at 450 °C and N\textsubscript{2} treatment at 250 °C led to a decrease in reverse currents. It would be interesting to perform these experiments with NH\textsubscript{3} plasma.

Improvement in luminescence intensity and fundamental changes of the radiative recombination after hydrogen plasma treatment have been observed in undoped and doped GaSb.\textsuperscript{259,267,268} PL measurements indicate that passivation of acceptors is more efficient than that of donors and, in general, the passivation efficiency depends on the doping level. The passivation efficiency is the highest for heavily Zn doped \textit{p}-GaSb. DLTS measurements carried out on \textit{n}-GaSb indicated decrease in deep trap concentration after hydrogenation. Extended defects like grain boundaries and dislocations are also found passivated. The most striking effect observed after hydrogenation was the efficient minority dopant passivation in these compensated samples. The depth profile of net donor concentration for an \textit{n}-GaSb sample co-doped with Te and Zn before and after hydrogenation is shown in Fig. 43. Since the material is \textit{n} type, one would expect the H to be in a negative charge state and thus not interact with acceptors. However, the increase in net donor concentration near the surface as depicted in Fig. 43 indicates the more efficient passivation of Zn acceptors compared to the Te donors in the co-doped \textit{n}-type samples.

The effective diffusion coefficient of hydrogen has been determined in \textit{n}\textsuperscript{+} and \textit{p}\textsuperscript{+} GaSb.\textsuperscript{257} Thermal reactivation of passivated shallow levels occurs around 200 °C. On the other hand, deep levels and extended defects are reactivated above 250 °C, indicating the higher thermal stability of the passivated nonradiative centres. The results of hydrogen passivation have been explained by assuming that hydrogen introduces a deep donor close to the valence band edge. In GaSb there is very little effect of hydrogen passivation on the electrical properties of the material, but drastic improvements are observed in the optical properties. This is beneficial for optoelectronic devices like lasers wherein the PL efficiency can be increased without affecting the shallow impurity level concentration.

C. \textit{a}-Si:H passivation

Our recent studies clearly demonstrated the effectiveness of \textit{a}-Si:H treatment in achieving bulk passivation due to
plasma hydrogen in addition to a defect-free surface termin-
ated by a-Si:H. Efficient passivation of point and extended
defects can be carried out by a-Si:H. Typical depth
resolved CL images recorded before and after passivation are
shown in Fig. 44. Effects of passivation is seen up to 3
μm in the bulk. With 10 keV beam, defects typical of melt
grown crystals like cellular dislocation network, twin bound-
aries, precipitates or impurity clusters can be seen in the
unpassivated sample (Fig. 44a). On passivation, the extended
defects are found passivated up to a thickness of 2.8 μm (see
Fig. 44b). However, with 20 keV beam (corresponding to a
depth of ~3 μm), the defects in the bulk are seen again as
they are not passivated (Fig. 44c). The CL and PL spectra
recorded on passivated samples exhibited higher lumines-
cence efficiency than the unpassivated ones. Most notably,
efficient passivation of minority dopant in Te compensated
p-GaSb is observed. This is similar to that observed in Te-Zn
codoped n-GaSb during hydrogen plasma passivation. The
passivation efficiency is found to improve with increase in
a-Si:H deposition temperature. The passivation of various
recombination centres in the bulk is attributed to formation of
hydrogen-impurity complexes by diffusion of hydrogen
ions from the plasma. a-Si:H acts as a protective cap layer
and prevents surface degradation which is usually encoun-
tered by bare exposure to hydrogen plasma. Thus for tech-
nological applications, a-Si:H treatment can be used as a
single step process through which both surface as well as
bulk defects can be passivated. Moreover, the process of
glow discharge is highly suitable for large scale device fab-
rication. The effect of a-Si:H buffer layer on the current
transport properties of GaSb Schottky diodes is discussed in
the following section.

IX. DEVICE ASPECTS

In this section, we focus our attention to the important
aspects of device fabrication technologies starting from wa-
fer preparation. The electrical and optical properties of vari-
ous device structures along with their possible applications
are discussed.

A. Wafer preparation

The successful preparation of a surface depends on the
proper cutting and abrasion processes followed by appropri-
ate chemical etching. Gatos, Lavine, and Warekois have
measured the depth of damaged layer in GaSb after mechani-
cal polishing. With abrasive particle size of 20 μm, the depth
of damage was 6 and 11 μm for the (111)A and (111)B
surfaces, respectively. The difference in the depth of damage
for the two surfaces is attributed to a distorted tetrahedral
structure on the (111)A surface.

A number of chemical etchants have been used for either
damage-free surface preparation or for defect characteriza-
tion. These etchants are listed in Table XI. GaSb requires an oxidising agent to break the bonds. Of the numerous oxidising agents that have been employed success-
fully, only HNO₃ and H₂O₂ have found widespread use for
various reasons involving etch rate, purity, mode of attack,
etc. Tervalent antimony that can exist in strong acid solu-
tions is easily hydrolyzed to antimonyl ions, which upon
dilution may precipitate as antimonyl oxy-salts. When at-
tacked by strong oxidizing agents, antimonides form the in-
soluble trioxide or pentoxide. To keep antimony in solution,
it is necessary to have a suitable complexing agent like HF,
HCl, tartaric acid, lactic acid, citric acid or oxalic acid. Most
of these complexing agents do not interfere with gallium.
Although specific ratios of components are given in Table
IX, the proportions can be varied with suitable adjustments
in etching time and temperature. For example, if the ratio of
HNO₃ to HCl is very large, insoluble antimony tri- or pen-
toxide forms while all other ratios yield soluble antimony
chlorides. Also ratios of HNO₃ to organic acids should be
kept low because strong acidic solutions suppress the ioniza-
tion of the organic acids which is necessary for them to act as
complexing agents. Due to the polar nature of the III–V
compounds, the etch rates on (111)A and (111)B are differ-
ent. Faust and Sagar found that the HNO₃ :tartaric acid
etchant attacks the antimony face of GaSb more rapidly than
the gallium face.

Electrolytic etching and polishing have proven invalu-
able in the manufacture of semiconductor devices. For GaSb,
electrolytic etching can be carried out using H₂SO₄:H₂O

FIG. 44. Panchromatic CL images of p-GaSb (a) as grown (10 keV), (b) treated by a-Si:H (10 keV) and (c) treated by a-Si:H (20 keV) (from Ref. 263).
Further, molten gallium at 500 °C has been used for alloy etching (100) surfaces of GaSb. Concentrated HCl can be used as a reagent for removing the alloying element. For obtaining atomically flat surfaces of GaSb prior to MBE growth, a large number of chemical etchants previously used for other III–V compounds has also been employed; however, a few have been found to be suitable. Smooth GaSb (100) surfaces can be produced by etching in HCl:H2O2:NaK (tartrate) (830 mM:300 mM:83 mM), HBr:HC1:HNO3:CH3COOH (1:10:15) and Br: methanol (5:1000) succeeded by heating in ultrahigh vacuum at temperature between 480–510 °C under an Sb flux. On the other hand, 2% Br2: methanol etching produces surface defects. Excellent reproducible atomically flat surfaces are produced by etching in CH3COOH:HNO3:HF (40:18:2) at room temperature for 40 s followed by HNO3:HCl (1:30) at 5 °C for 1 min. Also, HBr:HC1:HNO3 (0.9 M:0.8 M:0.04 M) in CH3COOH solvent followed by annealing in Sb flux at 550 °C for 15 min exhibited a flat surface with no traces of O2, least carbon contamination and a stoichiometric surface.

Controlled mesa etching for device structures can be carried out using NaK (tartrate)/HCl/H2O2 in various proportions. Etching rates in the range 0.1–1 μm/min can be obtained using different acid compositions.

For large scale device fabrication, high quality wafers with uniform properties are necessary. A recent study has shown that spatial CL imaging of GaSb wafers obtained from bulk as-grown crystals indicates that the luminescence centres (or defects) are distributed inhomogeneously. On annealing the wafers in Ga, Sb or vacuum, the centres get distributed homogeneously and the properties become uniform throughout the wafer. Amongst these, annealing in Ga has been found to be the most effective treatment.

B. Dry etching

Unlike in bulk wafer preparation, device applications require considerable advances in processing technology, including precision dry etching techniques. Compared to wet chemical etching, dry etching provides improved uniformity, greater repeatability, more anisotropic profiles, improved etch depth control and higher aspect ratios. Owing to high volatility of group III and group V chlorides, the most widely used plasma chemistry for III–V etching employs Cl discharges. Anisotropic dry etching of various III–V and their ternary and quaternary alloys has been achieved in high ion density electron cyclotron resonance (ECR) generated plasma by CH3/H2/Cl2/BCl3/Ar. The use of CH3/H2 for reactive ion etching (RIE) of III-V compounds offers several advantages when compared to other chemistries. Even though this has been demonstrated to be a universal etchant for various III–V alloys, to the best of our knowledge it has not been specifically tried on GaSb and related systems. The only work on dry etching of GaSb has been carried out by Pearton et al. 278 employing RIE with Cl2 and SiCl4. The etching rate is faster in Cl2/Ar than in SiCl4/Ar discharges, presumably because of more active chlorine species available in the former case. Average etch rates up to 8 μm/min have been achieved. After the RIE process, chlorine containing residues are left on the surface. The depth of this contamination is less than 20 Å and is always more prevalent for Cl2 than for SiCl4. However, the amount of surface residue is less than that obtained with conventional CC12F2 discharge.

The dependence of etched feature depth on the etching time for SiCl4/Ar and Cl2/Ar discharges is shown in Fig. 45a. The etching rate as a function of total pressure, plasma power density and Ar% are shown in Figs. 45b–d, respectively. The roles of these parameters on the etching behaviour have been discussed in detail by Pearton et al. 278

C. Atomically clean surfaces

Several methods have been used for preparing atomically clean surfaces like evaporated layers from the heated bulk, cleavage, heat treatment under high vacuum, ion bombardment and annealing, etc. Low energy electron diffraction (LEED) measurements on GaSb have indicated that heat treatment alone does not produce surfaces showing sharp diffraction patterns. Also, no diffraction patterns were obtained from the ion bombarded surfaces, indicating a disordered structure. Subsequent annealing at 400 °C for 30 min or more after ion bombardment resulted in sharp reproducible diffraction patterns.

The only adsorption studies made on clean surfaces of GaSb are that of oxygen, CO and CO2. The effects of exposing the cleaved-sputtered annealed (110), (111)A, (111)B and (100) surfaces to oxygen have been studied. The (110) surface was extremely inert with respect to the adsorption of oxygen. For the other surfaces, the oxygen presumably was adsorbed on the surface in a random arrangement or a polycrystalline oxide was formed. The adsorption of oxygen on the (111) Ga face proceeded at a faster rate (sticking coefficient \( \approx 10^{-4} \)) than on the (111)B (sticking coefficient \( \approx 10^{-5} \)). Oxygen could be removed from the GaSb by heat treatment at 350–400 °C. At these temperatures, diffusion of oxygen into the bulk has been shown by combined LEED and secondary emission measurements. No adsorption of CO occurs at room temperature on ion bombarded and annealed samples. Initial sticking coefficients of \( 10^{-6} \) and \( 10^{-5} \) for the CO2 adsorption on (111)B and (111) Ga surfaces of GaSb, respectively, have been obtained. The sorption of oxygen on GaSb has also been studied at 78 K and 26.2 °C. The amount of oxygen that is irreversibly absorbed at 1300 min at 78 K and 26.2 °C under oxygen pressure of 400 μTorr is \( 7.6 \times 10^{14} \) and \( 2.6 \times 10^{15} \) atoms/cm2, respectively. A low temperature (−250 °C) treatment using microwave ECR H2 plasma has been found to be effective in removing surface oxides from GaSb. 261

D. Fabrication techniques

1. Ohmic contacts

Ohmic contacts to p-GaSb doped in the range of \( 8 \times 10^{19} \) to \( 1 \times 10^{20} \) cm−3 are provided by thermal evaporation of several metals and alloys of Au, Ag and In after annealing in the range of 250–350 °C for 10–30 min. The specific contact resistivity \( \rho_c \) varies in the range of \( 10^{-4} \)–
TABLE XI. Chemical etchants for GaSb (compiled from Ref. 271). All formulas involving acetic acid are for glacial acetic acid (99.5%).

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Ratio</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HF:HNO₃:CH₃COOH</td>
<td>(2:18:40)</td>
<td>polishing effect</td>
</tr>
<tr>
<td>2</td>
<td>HNO₃:HF:CH₃COOH</td>
<td>(6:2:1)</td>
<td>polishing effect polycrystalline material cleaning</td>
</tr>
<tr>
<td>3</td>
<td>HF:CH₃COOH:KMnO₄ (0.05 M) (AB etchant)</td>
<td>(1:1:1)</td>
<td>impurity striations (high etch rate)</td>
</tr>
<tr>
<td>4</td>
<td>HCl:HNO₃:H₂O</td>
<td>(1:1:2)</td>
<td>dislocations on (111) A (slow etch rate)</td>
</tr>
<tr>
<td>5</td>
<td>HCl:30%H₂O₂:H₂O</td>
<td>(1:1:1)</td>
<td>solid–melt interface shape</td>
</tr>
<tr>
<td>6</td>
<td>HCl:HNO₃:H₂O</td>
<td>(1:3:6)</td>
<td>twins</td>
</tr>
<tr>
<td>7</td>
<td>HCl:H₂O₂</td>
<td>(1:1)</td>
<td>reveal dislocations, striations and microdefects</td>
</tr>
<tr>
<td>8</td>
<td>HCl:HF:H₂O</td>
<td>(1:1:1)</td>
<td>(for 15 s) dislocations and grain boundaries</td>
</tr>
<tr>
<td>9</td>
<td>HCl:CH₃COOH:H₂O</td>
<td>(9:5:1:10)</td>
<td>grain boundaries and dislocations</td>
</tr>
<tr>
<td>10</td>
<td>HCl:HF:H₂O</td>
<td>(1:1)</td>
<td>white spots at dislocations</td>
</tr>
<tr>
<td>11</td>
<td>HCl:CH₃COOH:H₂O</td>
<td>(2:1)</td>
<td>white spots at dislocations</td>
</tr>
<tr>
<td>12</td>
<td>HCl:HNO₃:H₂O</td>
<td>(1:1:1)</td>
<td>dislocations on (100) dislocations on (111) A</td>
</tr>
<tr>
<td>13</td>
<td>HCl:H₂O₂:tartaric acid</td>
<td>0.7:7.0:0.25 (molar ratio)</td>
<td>dislocations on (100)</td>
</tr>
<tr>
<td>14</td>
<td>HNO₃:HCl:CH₃COOH:H₂O</td>
<td>(5:3:11)</td>
<td>dislocations on (111)</td>
</tr>
<tr>
<td>15</td>
<td>KOH:H₂O</td>
<td>(9:11)</td>
<td>dislocations on (111)</td>
</tr>
<tr>
<td>16</td>
<td>HF:HNO₃:CH₃COOH:Br₂–CH₃OH</td>
<td>(1:9:20)</td>
<td>dislocations on (111)</td>
</tr>
<tr>
<td>17</td>
<td>45% aqueous KOH</td>
<td>(20:9:1)</td>
<td>dislocations on (111)</td>
</tr>
<tr>
<td>18</td>
<td>2% Br₂–methanol</td>
<td>(3:5:3:0.06)</td>
<td>dislocations on (111) A</td>
</tr>
<tr>
<td>19</td>
<td>HNO₃:HCl:CH₃COOH:Br₂</td>
<td>(20:9:1:1)</td>
<td>dislocations on (111) A</td>
</tr>
<tr>
<td>20</td>
<td>HNO₃:H₂O₂</td>
<td>(13:20:17)</td>
<td>stained cross-sectional view for p–n junctions</td>
</tr>
<tr>
<td>21</td>
<td>H₃O⁺:HCl:H₂O₂</td>
<td>(20:2:1)</td>
<td>stain etching on (110)</td>
</tr>
<tr>
<td>22</td>
<td>HNO₃:HCl:CH₃COOH:H₂O</td>
<td>(3:7:10)</td>
<td>p region etches more rapidly leaving a step at the p–n junction.</td>
</tr>
<tr>
<td>23</td>
<td>HNO₃:tartaric acid</td>
<td>(1:3)</td>
<td>dislocations on (111) A (etch rate: 6 mg/cm²/min)</td>
</tr>
<tr>
<td>24</td>
<td>HNO₃:HF</td>
<td>(1:1)</td>
<td>polishing effect (etch rate: 40 mg/cm²/min)</td>
</tr>
<tr>
<td>25</td>
<td>HNO₃:HF:H₂O</td>
<td>(1:1:1)</td>
<td>dislocations on (111) A (etching time: 30 s)</td>
</tr>
<tr>
<td>26</td>
<td>HNO₃:HF:HAc</td>
<td>(2:1:1)</td>
<td>dislocations on (111) A (etching time: 15 s)</td>
</tr>
<tr>
<td>27</td>
<td>HNO₃:HF:Br₂–CH₃OH</td>
<td>(5:3:3)</td>
<td>dislocations on (111) A (etching time: 30 s)</td>
</tr>
<tr>
<td>28</td>
<td>HNO₃:HAc:Br₂–CH₃OH</td>
<td>(25:15:15:3)</td>
<td>dislocations on (111) A (etching time: 10 s)</td>
</tr>
<tr>
<td>29</td>
<td>HNO₃:HAc:Br₂–CH₃OH</td>
<td>(1:1)</td>
<td>polishing effect (etch rate: 2 mg/cm²/min)</td>
</tr>
</tbody>
</table>
$10^{-6}$ Ω cm$^2$. Tadayon et al. fabricated metal contacts of Cr/Au, Ti/Pt/Au and Au on $p$-GaSb by MBE. For Au contacts, $\rho_c$ in the range of $1.4-7.8 \times 10^{-8}$ Ω cm$^2$ have been obtained which are the lowest values ever reported so far for $p$-GaSb. A critical surface preparation prior to metal contact was found to be necessary for achieving low contact resistivities. Prior to metallization, oxide layers were removed using (1:1) HCl:H$_2$O (for 30 s), followed by (1:1) buffered

FIG. 45. (a) Etched depth as a function of time and, average etching rate as a function of (b) pressure, (c) power density and (d) Ar % for RIE of GaSb in SiCl$_4$ (○) and Cl$_2$ (●) discharges (from Ref. 278).
HF:H₂O (for 30 s). Without this surface preparation, the ρ_r was found to be much higher (in the 10⁻⁶ Ω cm⁻² range). The effect of specific chemical etchants used for the surface etching prior to metallization on the leakage currents has been investigated by us (unpublished). It has been found that when the bulk substrates are dipped in HF for a long time, the Schottky diodes fabricated show capacitance transient which indicates a high conducting surface layer with carrier concentration of the order of 10¹⁷ cm⁻³ or more. This has been attributed to the increase in surface state density as reflected from the photoluminescence peak intensity and DLTS peak height of GaSb MOS structure. The preevaporation surface preparation for ohmic contact to the emitter and collector regions of heterojunction bipolar transistor consisting of oxygen plasma descum, 1 buffered HF:H₂O dip followed by de-ionized water (DI) rinse, and a final 1HCl: 1H₂O etch with DI rinse has been adopted by Anastasiou to obtain ρ_r of the order of 10⁻⁷ Ω cm².

To check the stability of the contacts, Tadayon et al. annealed the contacts in forming gas for 60 s. For the Au contact, the ρ_r decreases to 200 °C and increases thereafter. These diodes were further annealed at various temperatures for several hours. At higher annealing temperatures like 250 °C, ρ_r degraded to ~10⁻⁸ Ω cm² within 60 s. On the other hand, for low annealing temperatures such as 100 °C, the contact retained their low ρ_r even after 10 h. Milnes and co-workers found that the Ag contacts were stable for at least 100 h at 350 °C and may be expected to have little change over many thousands of hours at 70 °C. The Au based contacts however began to increase in resistance after 30 h at 250 °C. Ag is more stable than Au because the intermetallic compounds of Ag with Ga and Sb require a higher temperature for formation than the equivalent Au compounds.

Ohmic contacts on n-GaSb usually show higher contact resistivity compared to the p-GaSb ones. For contacts to n-GaSb, Au, AuTe or AuSn have been used with alloying at about 250 °C resulting in contact resistivities in the range 0.5–1×10⁻⁴ Ω cm². Au–Ge–Ni contact with 300 °C heat treatment for 5 min gives resistivities of the order of 10⁻⁵ Ω cm².

2. Schottky contacts

Rectifying metal–semiconductor contacts are basic devices in the technology of semiconductors. However, fabrication of ideal GaSb rectifying contacts has proved extremely difficult due to the oxidation of GaSb surfaces which is more serious than for Si, GaAs and InP. Schottky contacts on GaSb assume all the more importance for evaluation of its performance in epilayers due to lack of seminsulating substrates which have greatly obstructed the electrical characterization by Hall technique. Several metals have been used to fabricate Schottky contacts on n-GaSb. The barrier heights (at 300 K) are 0.65 eV (for Al), 0.6 eV (for Au, In, Pd), 0.5 eV (for Ga, Ni) and 0.42 eV (for Sb, Cr, Ag). Silver has been found to chemically react with Sb at the interface. Even though the Schottky barrier height mostly lies in a small range of values (0.5–0.6 eV), it depends on the preparation technique. For instance, in situ Al barriers on MBE-grown n-GaSb have given values of 0.54–0.56 eV compared to 0.65 eV for thermally evaporated contacts. From the barrier height measurements for several metals (Cs, Ga, Sb, Au) and oxygen coverages on (110) cleaved n-GaSb, Spicer et al. found that the Fermi level at the surface tends to pin slightly (~0.1 eV) above the valence band edge. There has been no independent check of the Fermi level pinning position for metals on p-GaAs as these contacts always show near ohmic nature and hence it is difficult to carry out reliable I–V or C–V measurements. With decrease in temperature, the barrier height increases indicating that the surface Fermi level tends to track the valence band edge. Pinning is less pronounced for metals that easily react with GaSb (like Sb) by forming chemical bonds even at low temperatures. Au selectively removes the Sb atoms from the interface and creates a highly nonstoichiometric interface region which becomes p-like to pin E_p at the valence band maximum. On the other hand Tan and Milnes found that Au contacts on GaSb deteriorate only after annealing above 350 °C for tens of hours. The mechanism of Fermi level pinning after metal deposition on GaSb (110) has been theoretically explained by a defect model by Nishida. The presence of atomic Ga at surface Sb vacancy sites, gives electronic states localized near the top of the valence band which can be responsible for the pinning. The ideality factor of the diodes usually varies in the range of 1.3–2.4. The high value of the ideality factor is attributed to the generation–recombination current from a near midgap center. The reverse currents of the Schottky barriers are governed by tunneling via midgap centers and surface leakage, or by band-to-band tunneling at higher voltages. As discussed in the previous subsection, surface passivation prior to metal deposition is beneficial and drastically improves the device characteristics like decrease in ideality factor and leakage currents, etc.

3. Oxides

Deposition of good oxides with low interface state density, high-resistivity, high breakdown field strength and suitable for high temperature processing is problematic for most III–V compound semiconductors, and GaSb is no exception to the rule. The interface state characteristics for native oxides of GaSb depend on the oxidizing process. The relationship of free Sb to interface states is not as established as for As at an oxide/GaAs interface. Wilsen in a study of nonaqueous anodic oxides concluded that there was no free Sb to interface unless the temperature exceeded 300 °C. Teare and Fischer evaluated the interface state density to be of the order of 10¹² cm⁻² for anodic oxides grown from KOH on (111)-oriented GaSb. A detailed study of the composition of thermal oxide on GaSb was carried out by Kitamura et al. by the x-ray photoelectron spectroscopic technique. They found that the oxide layer consists almost entirely of Ga₂O₃. A small amount of oxidized Sb generally exists at the crystal surface and a large amount of elemental Sb is located at the oxide–GaSb interface. Basu, Basu and Barman have carried out wet and dry O₂ oxidations to produce oxide layers of Ga₂O₃ and Sb₂O₃. They report interface state densities as low as 10¹⁰ cm⁻² eV⁻¹, electrical.
resistivities of 10^{10} \Omega \text{cm}^2 and breakdown field strengths of 10^6 \text{V/cm}. A treatment with ruthenium trichloride further improves the performance. The presence of Rb on the surface also enhances the oxidation rate of GaSb by six orders of magnitude with the formation of Ga_2O_3 and Sb_2O_5 at room temperature. p-GaSb surfaces are found to be more reactive than the n-GaSb ones suggesting the nature of the dopant to play an important at the interface. Very little work has been carried out on the deposition of SiO_2, Si(ON), or Al oxide, and the results are not encouraging.

4. Homojunctions

There exists very limited work in literature on the diffused homojunction structures. In the early 1960s, diffusion of In, Sn and Te was carried out (see Table X). Later in 1980, Capasso et al. fabricated p–n junctions using the LPE technique. Surface leakage was found to be the main problem. Recently, Polyakov et al. have reported improvements in the electrical properties of p–n junctions after sulfur passivation. Usually, for one-sided abrupt junctions with no fringing field, one would expect avalanche breakdown voltages of 10^{15} \text{cm}^{-3} and 2 V for a doping of 5 \times 10^{17} \text{cm}^{-3}. However, zinc diffusion in n-GaSb (Te doped: 3 \times 10^{17} \text{cm}^{-3}) at 680 °C for 4 h in flowing N_2 has led to breakdown voltages of 20–30 V with a wide p–type region of acceptor concentration of 5 \times 10^{15} \text{cm}^{-3}. The occurrence of the large width of this region may be due to reduction in native defects in undoped GaSb at high temperatures (\geq 600 °C), resulting in a high resistivity of the material. Such situations have been encountered during MBE growth of GaSb at 600 °C, and during LPE growth from Sb-rich solution.

GaSb light emitting diodes (LED) operating at room temperature were fabricated by a Zn diffusion technique. The peak electroluminescence emission wavelength was found to depend both on the LED drive current and the diffusion conditions used to produce the p–n junction. Longer diffusion periods resulted in diodes which emitted at shorter wavelengths.

Ion implantation in GaSb is much difficult compared to GaAs, GaP or InAs since at moderate to high doses, amorphization of the top layer takes place which is very difficult to anneal. Amorphous layer up to a depth of 1 \mu m has been observed. Further, it is seen that this layer develops small crystallites, dislocation loops and exhibit swelling after the annealing treatment. The threshold damage density for amorphization in GaSb is about 4 \times 10^{19} \text{keV/cm}^2 and the amorphous layer depth is about 65 nm for a 10^{15} \text{cm}^{-2} dose of Si at 20 keV. Efforts have been made to minimize the damage by varying the dose rate and accelerating voltage. Several species like Si, Mg, Ne, S, Se, Ar and Cs have been used for implantation. Least swelling (< 0.2 \mu m) is observed for a Mg^+ dose of 3 \times 10^{14} \text{cm}^{-2} and 300 keV.

Recently, we have observed p- to n-type conversion in the near surface region of GaSb as a result of argon-ion beam milling. Electron beam induced current (EBIC) measurements have been employed for detecting the type conversion. Enhancement in luminescence intensity is observed in regions where ion beam treatment occurs. The type conversion is proposed to occur due to a combined effect of generation of native donors (like Sb_{Ga} or V_{Sb}) and gettering of native acceptors originally present in the as-grown samples. The underlying mechanism that actually leads to the formation of the donor centres is yet to be understood. Nevertheless, for technological applications, the ion milling technique seems to be promising for the fabrication of reliable p–n junctions for photodiodes and other optoelectronic devices.

GaSb homojunctions normally have ideality factor of about 2.0 rising from traps near the centre of the band gap. The hole diffusion length in n-type bulk GaSb with doping concentration of 10^{17} \text{cm}^{-3} is usually in the range of 1–1.5 \mu m as measured by EBIC. The reverse characteristics are affected by large surface leakage currents. Auger processes that might influence recombination–generation in GaSb have been studied as a function of p-type doping and some usual characteristics have been observed due to large split-off in the valence band.

5. Heterojunctions

The degree of lattice matching is important in heterojunctions except for strained layers below the critical thickness. The critical thickness of GaSb(001)/AlSb structures has been shown to be 100–170 Å. For a lattice mismatch of as little as 3%, the interface state density may be greater than 10^{12} \text{cm}^{-2} which is sufficient to dominate the electrical properties. Moreover, the thermal expansion coefficients of the compounds are not the same and therefore lattice matching at the growth temperature may involve strain at normal device operation temperatures. LPE has been used for the growth of AlGaSb, GaAlAsSb and GaInAsSb on GaSb. The LPE growth of GaAlAsSb and InGaAsSb over a wide range of compositions is limited by the miscibility gap.

The phase diagram of AlGaAsSb has been described in great detail by Lazzari et al. The limitations of the solid phase composition have been discussed. The first limitation, which prevents the As introduction into the solid phase, is its low solubility in the liquid phase below 600 °C. The solubility is further reduced by the addition of Al in the melt. As a consequence of these low solubility values, GaSb lattice-matched Al_{1-x}Ga_{x}As_{y}Sb_{1-y} structures with x > 0.4 could not be grown below 600 °C. The AlGaAsSb system also suffers from the existence of an extremely wide solid phase miscibility gap. The binodal and spinodal curves at 500 and 615 °C are shown in Fig. 46. The dashed lines in the figure give the composition of AlGaAsSb lattice matched on GaSb. At 500 °C this line is (for a large part) located inside the thermodynamically metastable region of the miscibility gap. At 615 °C the miscibility gap is reduced and it becomes possible to obtain AlGaAsSb alloys in the stable domain in the whole range of composition. The intersection of the binodal curve and the lattice matched composition line gives the maximum values of x and y of the Al_{1-x}Ga_{x}As_{y}Sb_{1-y} lattice-matched alloys which can be grown in the stable region. This figure shows that high growth temperatures (>600 °C) are needed to obtain stable lattice-matched AlGaAsSb alloys in the entire range of composition.
AlGaAsSb with high Al content \((x = 0.82)\) has been carried out by us.\(^{333}\) The pregrowth dissolution cycles affect the morphology of the layers drastically. The optimum temperature to grow perfectly latticed-matched AlGaAsSb with \(x = 0.82\) has been found to be around 650 °C.

Due to the existence of a large solid phase miscibility gap, extending the operation wavelength of Ga\(_y\)In\(_x\)As\(_y\)Sb\(_{1-y}\)/GaSb lasers beyond 2 \(\mu\)m becomes difficult. It has been argued that growth inside an unstable region can still occur because the substrate tends to stabilize epitaxial layers which are nearly lattice matched. Lazzari et al.\(^{331}\) have discussed the growth limitations by the miscibility gap in the LPE of GaInAsSb on GaSb.\(^{333}\) Fig. 47 shows the binodal curves calculated with the hypothesis of stress-free solid phase (broken curves) and by taking into account the substrate-induced strain energy (solid lines). One can see a reduction in the total size of the miscibility gap of the system, and the existence of an extra miscible region for epitaxial layers with little or no mismatch. In that case, there is a solid phase stabilization by the substrate, and growth of Ga\(_y\)In\(_x\)As\(_y\)Sb\(_{1-y}\) alloy matched with GaSb is allowed in the whole domain of indium concentration \(0 < x < 1\) at 615 °C. It should be noted that the miscibility gaps are almost the same for strained (100) and strained (111) epitaxial layers.

MBE and MOCVD techniques have also been used for the growth of GaSb, InAs and AlSb based structures.\(^{334–339}\)

For lasers and waveguides where optical confinement is needed, knowledge of the refractive indices of the compound materials is required. The relative dielectric constant of GaSb is 14.44 and that of AlSb is 10.3. Hence (AlGa)Sb alloys can provide satisfactory confinement. The electron affinity of GaSb is 4.06 eV. Hence if large energy barriers are required, Al compounds have to be used. The band-gap energies and refractive indices of the quaternary compounds AlGaAsSb, GaInAsSb and InPAsSb lattice matched to GaSb have been calculated by Adachi.\(^{340}\)

The lattice-matching condition for the Al\(_x\)Ga\(_{1-x}\)As\(_y\)Sb\(_{1-y}\) on GaSb substrate is given by:

\[
y = 0.0396x/(0.4426 + 0.0318x) \quad \text{for} \quad 0 \leq x \leq 1.0.
\]

The lattice matching condition for the Ga\(_x\)In\(_{1-x}\)As\(_y\)Sb\(_{1-y}\) on GaSb substrate is given by:

\[
y = (0.3835 - 0.3835x)/(0.4210 + 0.216x)
\]

\[(\text{for} \quad 0 \leq x \leq 1.0).
\]

The lattice matching condition for the InP\(_x\)As\(_y\)Sb\(_{1-x-y}\) on GaSb substrate is given by:

\[
x = 0.6281 - 0.6895y \quad \text{for} \quad 0 \leq y \leq 0.91.
\]

Fig. 48a shows the band gap energies \((E_0, E_g^X \text{ and } E_g^L)\) and the refractive indices as a function of the composition for Al\(_x\)Ga\(_{1-x}\)As\(_y\)Sb\(_{1-y}\), lattice matched to GaSb. One can see from the figure that there is a direct-indirect transition around \(x \approx 0.45\). It is worth noting that the \(E_0\) value in the direct gap region of this system is very close to the lowest indirect gap energy \((E_g^X)\). This degeneracy of the conduction band at the \(\Gamma\) and \(L\) points is known to result in a large threshold current, owing to an injected electron loss in the

\(L\) valleys. The calculated refractive indices as a function of the photon energy with composition increments of 0.1 are shown in Fig. 48b. As can be seen from the figure, the AlGaAsSb/GaSb system provides a large refractive index step within a whole range of the \(x\) composition for the light confinement in an active region.

Fig. 49a shows the band gap energies \((E_0, E_g^X \text{ and } E_g^L)\) and the refractive indices as a function of the \(x\) composition for Ga\(_x\)In\(_{1-x}\)As\(_y\)Sb\(_{1-y}\) lattice matched to GaSb. Unlike AlGaAsSb, the absorption at the fundamental optical gaps in this system is expected to be direct within the whole range of the \(x\) composition. Moreover, the conduction band minimum at the \(\Gamma\) point is much lower than those at the \(L\) and \(X\) points, especially for smaller values of \(x\). The calculated refractive indices as a function of the photon energy with \(x\)-composition increments of 0.1 are shown in Fig. 49b. A noticeable feature found in this figure is that the system shows a refractive index anomaly, i.e., the smaller \(E_g^X\) gap material has a smaller value of the refractive index. Most of the III–V alloys like AlGaAs, InGaAsP and AlGaAsSb show the opposite trend. The origin of the refractive index anomaly has been discussed by Adachi. Since the refractive indices of
AlGaAsSb alloys are usually greater than those of GaInAsSb, cladding layers of AlGaAsSb make a strong combination with GaInAsSb active layer to confine radiation from such an injection laser.

Fig. 50a shows the band-gap energies \( E_0, E_g^X \) and \( E_g^L \) and the refractive indices as a function of the \( x \) composition for \( \text{InP}_{x-1}\text{As}_{1-x} \) lattice matched to GaSb. This quaternary has direct gaps as the fundamental absorption edges for the full range of the \( y \) composition. The direct gap values are much lower than the lowest indirect gap energies \( E_g^L \). The calculated refractive indices as a function of the photon energy with \( y \)-composition increments of 0.1 are shown in Fig. 50b. The refractive index anomaly occurs only in the region of smaller \( y \) composition \((y \leq 0.2)\). The long wavelength indices do not differ as much with the \( y \) composition. It is evident from this figure that InPAsSb lasers require an active layer of larger \( y \) and cladding layers of smaller \( y \) compositions in order to obtain sufficient optical confinement.

E. Device structures

1. Metal/a-Si:H/GaSb structures

Metal–semiconductor rectifying junctions have been traditionally used for both materials characterization and in device structures. As discussed in the previous subsection, obtaining ideal Schottky contacts on GaSb is difficult. The surface Fermi level in GaSb is pinned close to the valence band edge leading to extremely low Schottky barrier heights \((\sim 0.1 \text{ eV})\) on \( p \)-GaSb. This results in near ohmic behaviour of the metal/\( p \)-GaSb structure, thus limiting its applicability. The problems of low barrier height on \( p \)-GaSb and high leakage currents have been alleviated by modifying the semiconductor surface using thin interfacial layers prior to metallization.\(^{341}\) The interfacial layer can be an insulator, a larger band gap crystalline semiconductor or an amorphous
semiconductor. Amorphous semiconductors present many advantages compared to the other two and hence seems to be the best alternative.

The $I-V$ characteristics of the Mg/n-GaSb and Mg/a-Si:H/n-GaSb diodes for two interfacial layer thickness are shown in Fig. 51a. In the forward bias region, an increase in the turn-on voltage after the deposition of the interfacial layer can be seen. The turn-on voltage increases further with increase in the film thickness. In the reverse bias region, the diodes with interfacial layer exhibit excellent reverse current saturation, extremely low reverse current (~ tens of nA) and high breakdown voltage (~ 10 V).

The $I-V$ characteristics of various diodes fabricated on p-GaSb are shown in Fig. 51b. Systematic improvement in the diode characteristics is seen with increase in a-Si:H layer thickness. Good forward characteristics with reduction in reverse leakage current and breakdown voltage as high as 1.5 V are observed. Such $I-V$ characteristics would not have been possible in p-GaSb Schottky diode but for the interfacial layer. Moreover, the reverse current in these structures is lower than the p–n junctions fabricated previously. It is worth mentioning that even though the current flow in the forward bias regime will reduce due to series resistance of the a-Si:H layer, the same is not responsible for the increase in the turn-on voltage as depicted in Figs. 51a and 51b. The increased turn-on voltage has been explained in terms of the space charge limited current (SCLC) in the thin a-Si:H layer.

The current in these diodes are controlled by the barriers at the a-Si:H/GaSb and metal/a-Si:H junctions appearing in series with an effective resistance of the a-Si:H layer. From a technological point of view, since a rectifying metal/a-Si:H contact dominates the $I-V$ characteristic in reverse bias and low forward bias due to high barrier heights, GaSb based metal–semiconductor field-effect transistors (MESFETs) with extremely low gate leakage currents can be fabricated with interfacial layer of a-Si:H. Here the depletion layer extends through the a-Si:H layer into the bulk GaSb, allowing modulation of the channel in FETs. Furthermore, due to its ability to reduce leakage current, thin interfacial layers of a-Si:H can be potential surface passivants. Due to the extremely low dark currents, the a-Si:H/GaSb structures can also be employed as stacked solar cells of high efficiency.

2. Injection lasers

The (AlInGa)(As)n set of alloys have shown excellent device performance in the wavelength range of 0.8–2.3 μm. Optical pumping has been used to achieve room temperature laser oscillation at 2.07 μm in a GaInAsSb/AlGaAsSb double heterostructure on GaSb, however, the normal mode of interest is the pumping by injection current. In high-injection-current devices such as lasers, where substantial power is involved and temperatures must be kept low, the thermal resistance of the quaternary layers becomes important. The quaternary alloys have higher thermal resistivity than GaSb (3.3 cm K/W). Initially LPE-grown 2.2 μm laser structures exhibited room temperature threshold current densities of about 8 kA/cm². With improved growth conditions and using a different alloy composition, reduction in threshold current density to 3.5 kA/cm² at 290 K has been achieved.

Caneau et al. had grown GaInAsSb active layers with AlGaAsSb confinement layers by LPE as shown in Fig. 52 and demonstrated room temperature emission at 2.226 μm for pulsed operation with threshold current density as low as 1.7 kA/cm². Chiu, Zyskind, and Tsang also achieved similar threshold current density with MBE-grown InGaAsSb on (100) GaSb for emission wavelength in the 2–2.5 μm range. Room temperature cw operation of such LPE-grown lasers with confining layers more rich in Al has been demonstrated by Bochkarev et al. Eglash, Choi, and Turner and Eglash and Choi reported MBE-grown
GaInAsSb/AlGaAsSb lasers on GaSb with a threshold current density of 1.7 kA/cm² and differential quantum efficiencies of 18% per facet for pulsed operation at room temperature. GaSb-based diode lasers emitting at 2 and 4 \( \mu \)m with threshold current density as low as 260 A/cm² and cw output power of 190 mW/facet at room temperature have been fabricated by using cladding layers rich in Al content. High speed modulation of a GaSb/AlGaSb multiquantum-well laser diode up to 1 GHz for \( \lambda = 1.66 \) \( \mu \)m has been demonstrated by Toba and Nosu.\(^{351}\)

3. Photodetectors and solar cells

The ratio of ionisation coefficients of holes and electrons \((k_p/k_n)\) is large and is a key factor for high speed, low noise avalanche photodetectors (APDs). The high ratio of ionisation coefficients as shown in Fig. 53 can be observed in Ga\(_{1-x}\)Al\(_x\)Sb structures with \(x\) in the range of 0.04–0.06.\(^{352-364}\) Minimum in the threshold energy for impact ionisation near \(\Delta \approx E_g\) composition cannot explain enhancement of hole ionisation coefficient. Increased scattering rate is responsible for this enhancement which is caused by a minimum change of momentum in the hole ionisation near the threshold and the mixing of a S-like state with the valence-like state induced by a composition disorder in this ternary compound. The dark current of such diodes tends to be largely due to generation in the space charge region and by tunnelling through deep centres at high reverse voltages. Reduction of deep impurity centres and native defect concentration during growth has helped in minimizing the tunnel current. Avalanche multiplication factors of 30–50 with external quantum efficiencies of over 50% at 1.3 \(\mu\)m and a sensitivity of 0.6 A/W have been obtained. A \(p^+n\) Al\(_{0.053}\)Ga\(_{0.947}\)Sb homojunction avalanche photodiode for 1.7 \(\mu\)m detection has demonstrated a gain of 30 with an excess noise factor of 3.8 dB which is better than that of an InGaAs APD.\(^{358}\) The structure and reverse \(I-V\) characteristics of such an APD are shown in Fig. 54. A detector fabricated from an \(n^-Ga_{0.82}In_{0.18}As_{0.17}Sb_{0.83}\) layer with Zn diffused \(p^+\) face has...
exhibited rise and fall times of about 50 and 500 ps and the detector response to pseudomodulation at bit rates up to 2 Gbit/s.363

IR detectors in the 8–14 μm regime are presently fabricated by the mercury based compound HgCdTe which is extremely difficult and hazardous to manufacture. At present, the Sb-based III–V are under intense investigation for detectors in this range. Detection of longer wavelengths, 8–14 μm, is possible with intersubband absorption in Ga1−xAlxSb/AlSb superlattices.4 The novel type II strained-layer superlattice system of InAs-InGa1−xSb also shows promise as material for infrared detection in the 8–14 μm range.365 In this system, the two constituent layers are not lattice matched. The internal strain effects caused by the mismatch are used to reduce the band gap of the InAs quantum wells. Calculations show that the InGa1−xSb–InAs has an effective mass greater than and absorption comparable to that of Hg1−xCd1−xTe (MCT). The quality of the superlattices is highly dependent on growth conditions. Substantial improvements in structural quality can be achieved by growing the superlattice structures on GaSb substrates; however, GaAs substrates are less expensive and provide the possibility of monolithic integration with readout circuitry. Hence, it is desirable to have the superlattice structure on a GaSb buffer layer grown on GaAs substrate. Unfortunately, the lattice constant of GaSb is 7% larger than that of GaAs, causing large concentrations of dislocations at the interface. To overcome the lattice mismatch problem, thick stress-relaxed buffer layers of GaSb on (100)-oriented GaAs substrates have been grown with a short-period heavily strained superlattice at the interface of GaAs/GaSb. An absorption coefficient of 2000 cm−1 at 10 μm has been measured from such a superlattice with an 11 μm energy gap. This value is comparable to that of bulk MCT, the current industry standard for IR detectors in the 8–14 μm range.365

p+−InSb/π-InAs1−xSbx/n+−InSb heterojunction photodiodes operating at room temperature in the 8–13 μm region have recently been reported by Kim et al.366 The voltage responsivity-area product of 3 × 10−5 V cm2/W has been obtained at 300 K for the λ = 10.6 μm optimized device. This is close to the theoretical limit set by the Auger mechanism, with a detectivity at room temperature of ≈1.5 × 108 cm Hz1/2/W.

GaSb p+n solar cells have been proposed as units to be placed behind GaAs solar cells. At 50× light concentration and air mass zero (AM0) the GaSb cells exhibit 6.5% efficiency which under favourable conditions might boost the efficiency of a GaAs/GaSb tandem stack to over 30%.15 In order to use a single load, the current in the tandem solar cells have to be matched. However, because of the difficulty in obtaining matching conditions over a large range of input illumination, the applications of GaSb solar cells are limited. Reduced series resistance in future GaSb cells by improved contact metallization and a denser grid design will allow tandem solar energy conversion efficiencies over 35%. GaSb TPV cells coupled with a gas-fueled burner have already demonstrated 27% efficiency at a loading of 13 W/cm2 in a geometry amenable to automotive applications.57 Further improvements can be achieved by using the Ga0.9In0.1Sb alloy.

Charge storage and charge transfer in a AlGaAsSb/GaSb heterojunction charge coupled device (CCD) have been demonstrated by Liu et al.367 A charge filling time as long as 450 s has been observed at 77 K. Room temperature operation has not been possible due to high leakage current in the device.

4. Transistors

The performance of bipolar and FETs of (AlInGa)(AsSb) has been evaluated by several
workers. The GaSb/InAs heterojunctions are of the broken gap variety as the valence band edge of the GaSb lies above the conduction band edge of the InAs (see Fig. 55). Therefore near-ohmic behaviour and tunnelling occurs unless Al is included in the GaSb to create a staggering junction interface. Such a structure as shown in Fig. 56 with an AlSb emitter, an InAs base and a GaSb collector has been fabricated by Chui and Levi. The best collector efficiency obtained was about 0.9. Taira et al. fabricated two hot electron transistors (HET) with a p-GaSb emitter/n-InAs base/p-GaSb collector and with GaSb emitter/InAs base/graded Ga0.9Al0.1Sb collector. In the latter structure, a current gain of 6 was obtained at 300 K. Furukawa and Mizuta fabricated a heterojunction bipolar transistor (HBT) with n-Al0.5Ga0.5Sb emitter/p-GaSb base/n-GaSb collector. Fig. 57 shows the structure and I–V characteristics of the HBT. At 300 K, the hole mobility in the base was three times better than that for similar doping concentration of GaAs and the gain was as high as 160 for a 100 μm 2 size emitter. The AlGaAs/GaAsSb strained system has desirable properties for high-current-gain high-frequency HBT applications. GaAsSb has been shown to facilitate p-type ohmic contacts to p–n–p AlGaAs/GaAs HBTs with specific contact resistance as low as $5 \times 10^{-7} \, \Omega \cdot \text{cm}^2$. A prototype $n$–$p$–$n$ AlGaAs/GaAsSb/GaAs DHBT exhibited a stable current gain of 5 and a significant collector current density of $5 \times 10^4 \, \text{A/cm}^2$. GaSb $p$-channel modulation-doped FETs (MODFETs) with AlSb$_{0.9}$As$_{0.1}$/AlSb barrier layers have been studied by Luo and co-workers. For 1 μm gate length devices the transconductances were 50–86 mS/mm at 77 K. The schematic cross section and band diagram of the MODFET are shown in Fig. 58. Longenbach and co-workers proposed a complementary heterojunction FET (HFET) structure with InAs as the $n$ channel and GaSb as the $p$ channel. The structure is shown in Fig. 59. Complementary FET pairs of such types have been studied by Kanji et al. FETs using InAs active layer and GaSb or AlSb barrier layer have been fabricated by Kop’ev et al. and Werking et al. With a gate length of 1.7 μm, the transconductance of an InAs channel FET has been found in the range of 460–500 mS/mm at room temperature.

Quantum wells (QWs) of InAs with (AlGa)(AsSb) barriers combine the high intrinsic mobilities ($\simeq 30,000 \, \text{cm}^2/\text{V} \cdot \text{s}$) and the high drift velocities in InAs ($\simeq 4 \times 10^7 \, \text{cm/s}$ at 2.5 kV/cm), with the high electron confinement barrier (1.35 eV) of the InAs–AlSb interface. These two sets of properties are promising for InAs based HFETs with superior speed compared to other materials. While actual device performance still falls short of theoretical expectations, with 0.5 μm gate length, cutoff frequency of 93 GHz has been demonstrated.

The three terminal resonant interband tunnelling FET (RITFET), based on type II InAs/AlSb/GaSb RITD integrated into the drain or source region of an InGaAs/AlGaAs/ GaAs FET (see Fig. 60) demonstrates the possibility of combining the best tunneling diode structure with the best of the FET technology to achieve the highest possible peak to valley (P/V) current ratio and gain for future quantum three terminal devices.

5. Quantum wells, quantum dots and superlattices

Way back in 1980, Chang and Esaki demonstrated tunneling actions in InAs–GaSb superlattices. Semiconductor–semimetal transition is observed in InAs–GaSb superlattices. The critical layer thickness for this transition is calculated to be 85 Å, below which the superlattices...
behave as semiconductors and above which semimetals. More recently, several researchers have fabricated tunnelling devices based on the InAs–AlSb–GaSb QW structures and studied their transport properties.381–400 Ten different tunnel structures are realizable by employing this system as shown in Fig. 61.381–393 The optical properties of QWs and superlattices involving AlGaSb have been found to be interesting for device applications specially for long wavelength detection. Forbidden Auger process in strained InGaSb/AlGaSb QWs has been studied by Jiang and co-workers.396 Carr et al.397 made an analysis of the quantum-confined stark effect in GaSb/AlGaSb multiple QWs (MQWs). A normal-incidence modulation is proposed which uses the Stark effect to induce Γ–L transitions in asymmetrically stepped AlSb/InAs/GaSb/AlSb QWs.398 The calculations indicate that on/off ratios can be achieved in this structure operating at \( T \leq 150 \text{ K} \) with electric fields on the order of \( \sim 100 \text{ kV/cm} \) for any infrared wavelength within the range of 3–20 \( \mu \text{m} \). Electron transfer from \( \Gamma \) to \( L \) valleys, and hence the device switching, can be achieved efficiently under a moderate bias (see Fig. 62). Infrared devices based on this system can potentially operate at both long-wave (8–12 \( \mu \text{m} \)) and mid-wave (3–5 \( \mu \text{m} \)) infrared ranges, due to the large \( L \) valley offsets of InAs and GaSb with AlSb.

In GaSb, due to the proximity of the \( L \) conduction band to the \( \Gamma \), for (001) grown QWs or superlattices, the effective mass tensor is nondiagonal allowing normal incidence electronic intersubband transitions. \( L \) valleys can be populated either through confinement by adding Al to GaSb or through high doping and strong far infrared absorption at normal incidence is observed. This is attractive for infrared detectors.

![Figure 57](image1.png) **FIG. 57.** Hot electron emitter transistor, (a) conduction band arrangements of emitter and base (\( \Gamma \) and \( L \) valley minimum values of \( \text{Al}_{0.6}\text{Ga}_{0.4}\text{Sb} \) are not so different and they are shown by single broken line), (b) common-emitter \( I–V \) characteristics for the AlGaSb/GaSb HBT at 300 K. Base current is 20 \( \mu \text{A} \)/step (from Ref. 372).

![Figure 58](image2.png) **FIG. 58.** GaSb \( p \)-channel MODFET. (a) schematic cross section; (b) band diagram at zero bias (from Ref. 373).

![Figure 59](image3.png) **FIG. 59.** (a) Band diagram of a complementary HFET structure of InAs/AlGaSb/GaSb; (b) cross section of InAs/AlGaSb/GaSb complementary HFET integrated circuit (from Ref. 374).
modulators and second harmonic generation (SHG), etc. Surface emitting SHG at normal incidence using $L$ valley intersubband transitions in AlSb/GaSb/GaAlSb/AlSb stepped QWs has been demonstrated. Second harmonic susceptibility of at least $9 \times 10^{-8}$ m/V has been achieved under double resonance conditions, which is comparable to the best obtainable with $\Gamma$ valley processes in GaAs/GaAlAs systems for $45^\circ$ propagation angles. Besides the advantage of normal incidence geometry, the large $L$ valley conduction band offset between GaSb and AlSb enables doubling of frequencies spanning the entire midwave infrared spectral region. For an Al$_{x}$Ga$_{1-x}$Sb/GaSb QW with barrier composition of $x = 0.31$, the confinement induced $\Gamma$–$L$ crossover occurs at a well thickness of 12 monolayers.

In GaSb/AlSb quantum wells, “quasidirect” transitions from the $X$ conduction band to the $\Gamma$ valence band in the GaSb is possible provided its thickness is only a few monolayers. PL characteristics at 1.4 K suggest that the interband selection rules for $k$ conservation are relaxed in such narrow QWs. Optically induced femtosecond electromagnetic pulses from GaSb/AlSb strained-layer superlattices were observed by Zhang et al. GaSb–AlSb MQWs are “good relaxed systems” and structures grown on GaAs substrates are of good optoelectronic quality. The difference in optical index of GaSb and AlSb is about a factor of 2 better than that between InP and InGaAsP quaternary alloy. It is known that it requires 20 pairs of InP/InGaAsP layers to achieve a reflectivity of only 95%. GaSb–AlSb MQWs have one excitonic absorption line peaking at about 1.5 $\mu$m at room temperature and a 10 pair Bragg reflector shows 97% reflectivity. This will prove useful for microcavity based devices such as vertical cavity surface emitting lasers.

Magnetic field induced semimetal and semiconductor transition in InAs–GaSb superlattices has been observed by Kawai et al. with closely overlapped subbands of electrons and holes. The transition is manifested in a sharp increase in the magnetoresistance in the quantum limit, where the ground Landau levels associated with the subbands are...
crossed at the Fermi level, resulting in carrier depletion. The InAs–GaSb system is known to exhibit unusual magnetotransport properties arising from coexisting two-dimensional electrons and holes which result from the peculiar band offsets at the interface between the two materials and with an electron mobility of $3.5 \times 10^6 \text{cm}^2/\text{V s}$ in the presence of holes. The holes disappear at a critical InAs thickness around 60 Å resulting from the semimetal–semiconductor transition.\textsuperscript{404}

Sb/GaSb(111) heterojunction and multilayers structures are potential systems with indirect narrow gap superlattice, where spacial quantization effects induce a positive valence–conduction band energy gap in the Sb semimetal layers and the large characteristic lengths in the Sb layers can be exploited for the study of size quantization effects. The transport and optical properties of such structures have been investigated by Golding et al.\textsuperscript{405} Sb/GaSb quantum wells and superlattices may be ideal system for studying quantum transport and electron–hole correlation effects. Taking bulk values for the electron and hole densities ($\sim 10^{19} \text{cm}^{-3}$) and low temperature mobilities ($\sim 10^8 \text{cm}^2/\text{V s}$), one obtains mean free paths of nearly 10 $\mu$m. One also expects that the Auger recombination lifetime should be orders of magnitude longer than in direct gap semiconductors with the same band gap. The large mass anisotropy, multiple conduction and valence minima, long lifetime and small absorption coefficient across the indirect gap are all highly favourable for nonlinear optical applications, such as optical switches devices operating in the infrared.

Self-assembled nanoscale quantum dots of GaSb were grown on GaAs (001) by MBE.\textsuperscript{406–409} In situ scanning tunnelling microscopy measurements taken after 1–2 monolayers growth of GaSb reveal that the surface is a network of anisotropic ribbonlike platelets. These platelets are a precursor to quantum dot (QD) nucleation. Transmission electron microscopy measurements indicate that the QDs are coherently strained. The growth of these QDs occurs via Stranski–Krastanov mode. QDs of GaSb capped by GaAs exhibit strong luminescence near 1.1 eV. This line is attributed to radiative recombination of 0-D holes located in the GaSb dots and electrons located in the surrounding regions.

X. CONCLUDING REMARKS AND FUTURE OUTLOOK

The usage of GaSb based systems as an alternative to the present day devices operating in the 1.55 $\mu$m and for sources and detectors in the 2.5 $\mu$m regime relies on the production of high quality material with low background doping level and defect density. While the basic material quality is dictated by the crystal growth conditions, the physical properties of the material are profoundly influenced by the processing cycles and the conditions under which the device is operated. Hence in making a good device, it is important to understand the material issues that are related to device fabrication and device operation and to achieve synergies between material preparation, processing and device functions.

A comparison of the problems encountered by early workers during the developmental stages of other III–V or II–VI optoelectronic materials and GaSb indicates that there is relatively less hinderance for bringing out the full potential applications of the latter system. There are several special basic properties of GaSb and related materials that can be immediately exploited for large scale commercially reliable devices.

High quality device grade bulk substrate can be produced more suitably by vertical Bridgman with submerged heater\textsuperscript{410} and vertical gradient freeze methods rather than conventional Czochralski technique. Materials produced by these techniques have shown the lowest defect content and are commercially viable. The stacking fault energy of GaSb is highest amongst III–V and the critical resolved shear stress (CRSS) is relatively higher; hence, obtaining low defect density crystals is relatively easier. Further, even though lot of efforts have been made to grow bulk crystals from Ga- or Sb-rich melts with low native background acceptor levels, it is disadvantageous from the structural quality point of view. Metallic inclusions that get introduced during nonstoichiometric melt growth can limit the usefulness of the bulk crystals as substrates. Instead, the best ways to circumvent the high background doping level, which may affect the device performance, can be either by postgrowth Li diffusion or by epitaxial growth of GaSb buffer layer on the bulk substrate. High quality epilayers can be grown by LPE, MOCVD or MBE with native acceptor concentrations two orders of magnitude lower than the bulk.

Even though there exists substantial understanding about the physics of the material, there are several avenues where further work has to be carried out in order to upgrade this III–V system for optoelectronic devices. Some of the areas that need immediate attention are discussed below.

Doping of impurities has been restricted to only a few elements. A rigorous study on doping of various impurities should be carried out, first to see the effects of dopants on the native defects and second to obtain carrier concentration which can be varied from the intrinsic concentration limit to very high levels $\sim 10^{20} \text{cm}^{-3}$. Various doping levels may be possible with different impurities. Also, the spectrum of defect levels for various impurities has to be determined. Codoping may lead to interesting material properties and device applications. Isoelectronic dopants may reduce native defects considerably.

Ion implantation and diffusion of impurities need to be worked on more carefully and attempts should be made to solve the problems encountered previously. Luminescence from impurity levels in the band gap may prove promising in exploiting this material as IR sources. Hence, optical characterization of various luminescence centres should be carried out in detail. Attempts to increase carrier mobilities have to be made by suitably defect complexation mechanisms. DX-centre based basic research and device applications may prove useful using S:GaSb rather than conventional AlGaAs. A theoretical analysis to this effect in GaSb is also essential.

High resistivity substrate (with intrinsic resistivity limit) is of utmost importance. Even though some indications of high resistivity GaSb through high temperature annealing\textsuperscript{313}...
or by Te compensation have been given, such a study is yet to be pursued rigorously. Since the band gap of GaSb is comparatively low, the intrinsic resistivity limit is of the order of 10$^3$ Ω cm. Unlike in wide band gap III–V like GaAs and InP where high resistivity can be achieved by creating midgap levels, such an approach has not been successful until now in GaSb. Sulfur can be an interesting dopant as it is a deep trap (DX centre) which can reduce the carrier concentration by three orders of magnitude from 10$^{17}$ to 10$^{14}$ cm$^{-3}$ with decrease in temperature from 300 to 77 K. Ion beam milling can also be adopted to reach the level of intrinsic resistivity.

Both hydrogen plasma passivation and proton implantation can be used to produce current confining regions in double heterostructures lasers with AlGaAsSb cladding layers. n- to p-type conversion of AlGaAsSb has been observed by proton implantation. Hydrogen passivation seems to be more advantageous than proton implantation if one aims at producing narrow stripe lasers for high frequency applications because the isolation is provided by high resistivity regions rather than by p–n junction formation.

The problem of high leakage current in devices can be eliminated by effective passivants like S, Ru and a-Si:H, which have been found to be robust. Further work is necessary to employ these surface passivation techniques for the batch on-line device fabrication cycles. Also, basic device technologies like wafer preparation, oxide growth, metallization, etc., have to be standardized. Long term stability over many thousands of hours at the highest operating temperature is a matter of considerable importance for contacts. Contact technology is not yet fully developed. Extended testing is needed to develop firm data on the 100 °C lifetime.

Until now, most of the GaSb based work has been on bulk crystals. Despite promising device capabilities, the epitaxial technology is highly under-utilized. Material preparation using sophisticated epitaxial techniques like MOCVD and MBE should be pursued and their properties studied. Initial problems encountered in epitaxial techniques need to be solved by knowledge gathered from GaAs and InP. A typical example is of LPE growth of GaSb from Sb-rich melt wherein the problem of bad surface morphology usually encountered may be solved by the doping of rare earth elements to the melt.

Preliminary efforts in bulk growth of GaSb based ternaries (InGaSb and AlGaSb) have shown encouraging results. If succeeded, this will drastically reduce the cost of GaSb based optoelectronic devices and make it a much more feasible technology compared to the existing ones. Rigorous characterization of such material systems should be carried out for further advancement.

From device point of view, GaSb based ternary and quaternary heterostructures exhibit interesting optical properties for sources and detectors in the 1.3–2.5 μm regime. In spite of several important properties, Sb based compounds have lagged behind in the past due to several reasons. Lack of suitable substrates and their large lattice mismatch to GaAs and InP is one. The existence of large miscibility gaps precludes the growth of high quality materials at lower temperatures by equilibrium and nonequilibrium techniques. On the other hand, because of their low band gaps, the transport properties are expected to improve considerably at low temperatures and therefore these materials and devices would be important for cryogenic applications. However, epitaxial materials grown by MBE exhibit type conversion and degradation of the transport properties as the measurement temperature is lowered from 300 K. In terms of the final device structure, it is envisaged that GaSb layers would form the buffer and contact layers; Ga$_{1-x}$In$_x$As$_{1-y}$Sb$_{y}$, the active layers for lasers and detectors in the 2–4 μm regime and Ga$_{1-x}$Al$_x$As$_{1-y}$Sb$_y$, the cladding layers. Since the Fermi level is pinned close to the valence band edge in p–GaSb, it forms an excellent ohmic contact material on wide band gap III–V compounds.

The present day APDs based on InGaAs/InP for 1.3–1.55 μm light wave communication systems can be replaced by AlGaSb/GaSb APDs, which have lower excess noise factor and higher gain–bandwidth product than the former. Gain–bandwidth product of 90 GHz has been demonstrated which is the largest ever reported for long wavelength APDs.

In comparison to the present day HgCdTe detectors for 8–14 μm regime, the InAs/Ga$_{1-x}$In$_x$Sb superlattices are expected to hold several advantages:

(i) a higher degree of uniformity, which is crucial for the fabrication of large infrared detector arrays;
(ii) smaller leakage current due to the tunable increase in effective mass available in a superlattice;
(iii) reduced Auger recombination rates, due to the substantial splitting of the light and heavy hole bands and the increase in electron effective mass;
(iv) better understood device processing techniques; and
(v) compatibility with GaAs-based readout electronics.

Furthermore, the performance of infrared detectors based on In$_x$As$_{1-y}$Ga$_{1-x}$In$_y$Sb superlattices is not limited by the high thermal generation rates which preclude large $D^*$ in multi-quantum well infrared detectors (such as GaAs/AlGaAs). The other candidate, In$_x$As$_{1-y}$Sb$_y$, also exhibits several important advantages over Hg$_{1-x}$Cd$_x$Te like better stability, higher electron and hole mobilities, high quality and low cost substrates like GaAs. The performance of these detectors can be further improved by optical immersion with lenses prepared directly from the GaAs substrate similar to what has been done for HgCdTe devices. Recent advances in GaSb and InGaSb TPV technology indicate a favourable future market trend.

As far as the sources are concerned, further improvement may be expected in GaInAsSb injection laser performance since many features found in GaAs laser structures have not yet been thoroughly explored. This includes quantum wells and graded index confining layers to improve the linewidth and efficiency.

Intraband and interband negative resistance tunnel devices with high peak-to-valley ratios and FETs have promising features for high speed applications.
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13 See the NETSCAPE homepages: NASA highlights, diode laser gas sensors, etc.
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