Investigation of Electrical and Optothermal Properties of Si-doped GaSb epitaxial layers by the Hall Effect, PL measurement and Photothermal Deflection Spectroscopy

S. Abroug(a) *, F. Saadallah(a), F. Genty(b), N. Yacoubi(a)

(a) photothermal laboratory IPEIN, BP 62, Mrezka 8000, Nabeul, Tunisia,
(b) IES, univ-montpellier 2, France

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Abstract

The aim of this work is to investigate the influence of Si-doping on the optical, thermal and electrical properties of GaSb epitaxial layers. Such an influence was quantified through photoluminescence (PL), mirage effect (photothermal spectroscopy) and Hall effect measurements. Several GaSb samples, grown by Molecular Beam Epitaxy (MBE) on (100)-oriented GaAs semi-insulating substrates, with different Si-doping levels ranging from $4.9 \times 10^{16}$ at.cm$^{-3}$ up to $8.1 \times 10^{19}$ at.cm$^{-3}$ were tested. As a comparison, the same measurements were also performed on a GaSb non intentionally doped layer. The Hall effect data shows a monotonic decrease in carrier mobility when the hole concentration increase.

The effect of band-to-band, band-impurity transitions on the PL gap $E_0$ and the influence of high impurity concentration on the PL and absorption spectra have been also studied. Finally, the optical absorption changes induced by Si-doping on GaSb samples were investigated by photothermal deflection. It was shown that this technique allows a very precise deduction of the real interband gap energy of a semiconductor material as GaSb.

Thermal conductivities were also deduced from the photothermal deflection measurements. The found values are very low due to the thermal resistivity of the layer-substrate interface but also due to the lattice-mismatch between GaSb epilayers and the GaAs substrate. However, the contribution of the free carriers to the thermal conductivity, with a high p-doping level ($p > 10^{19}$ cm$^{-3}$), could be highlighted.

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1. Introduction:

GaSb and its related ternary and quaternary alloys have been considered as promising materials for optoelectronic device application (e.g. lasers and photo detectors) in the near and middle infrared wave-length range [1]. The

* Corresponding author. Tel.: +0-216- 97-529-720; fax: +0-216-72-220-181.
E-mail address: abrsouma@yahoo.fr.

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electrical, thermal and optical properties of semiconductors are significantly modified when heavy doping conditions occur. However, in device application, GaSb with higher p-type doping is required to form ohmic contacts. Only few studies about the p-type doping of GaSb epitaxial layers have been published [2, 3].

It has been found that the optical and electrical properties of GaSb are strongly dependent on the doping concentration and growth conditions [4, 5].

The heavy doping affects the density of states, carrier mobility, absorption, band structures, luminescence properties and hence the device performance [6, 7]. In addition, the high doping affects the band gap shrinkage and the band tail extending into the gap. In the heterojunction-based devices, the band gap shift, due to heavy doping, results in a valence and conduction band discontinuity at the heterojunction interface [8]. Low temperature photoluminescence (LTPL) is a common technique used to investigate the band structures of GaSb at high doping levels. The luminescence properties are dependent on the growth conditions, doping concentration, impurity species and growth temperature. In this paper we have reported the results from LTPL properties of Si–doped GaSb while varying hole concentration, growth temperature, and measurement conditions. This study suggest a relationship between full width at half maximum (FWHM) and band gap of Si-doped GaSb which could be considered as a useful tool for determining the hole concentration in Si-doped GaSb. Finally, we used the photothermal deflection spectroscopy to determine the absorption spectrum and the band gap energy, which will be compared to the PL measurements.

2. Experimental Setup

All the samples were grown in a Ribert MBE system from elemental gallium and antimony sources, the doping concentrations and hole mobility were determined by Hall Effect measurements at room temperature. PL measurements were carried out using a Fourier Transform PL system, using laser at a temperature ranging from 97 K to 300K. Laser diode operating at a wavelength of 650nm with 82.2 mW power, was used as a source of excitation. PL signal was detected by an InSb detector operating in the range of 1.24 - 0.24 eV. The technique of photothermal deflection spectroscopy is described in detail elsewhere [9, 10]. The sample is heated using a 250 W halogen lamp placed behind the slot of a monochromator. Light coming out of the monochromator is chopped using a mechanical chopper. The energy absorbed by the sample generates a thermal wave which propagates into the surrounding fluid leading to a refractive index gradient, causing the deflection of a probe laser beam skimming the sample surface. The deflection is measured by a position photodetector linked to a lock-in amplifier. The obtained photothermal signal could be related to optical and thermal properties of the sample.

3. Results and discussion

Molecular Beam Epitaxy (MBE) and metal organic chemical vapour deposition (MOCVD) are the preferred techniques to grow this structure in order to meet the stringent compositional and thickness requirements [11]. The characteristics of the studied epitaxial layers grown by MBE on semi-insulating (100) GaAs substrates, are shown in the table 1:

| Sample | GaSb (n.i.d) | GaSb (Si) | GaSb (Si) | GaSb (Si) | GaSb (Si) | GaSb (Si) |
|-------|-------------|-----------|-----------|-----------|-----------|-----------|
| Temperature of growth (°C) | 560 | 700 | 1080 | 1150 | 1250 | 1300 |
| Thickness (μm) | 1.8 | 2.2 | 2.3 | 2.3 | 2.1 | 2.2 |
| Hole concentration (cm⁻³) | 2.1 \(10^{16}\) | 4.9510\(10^{16}\) | 3.4310\(10^{17}\) | 2 \(10^{18}\) | 2.310\(10^{19}\) | 8.11 \(10^{19}\) |
| Hall mobility (cm²/V-s) | 368 | 556 | 478 | 343 | 179 | 137 |
| Resistivity (Ω-cm) | 0.8067 | 0.2268 | 0.03814 | 0.009054 | 0.00152 | 0.0005637 |
| Electrical Conductivity (Ω⁻1-cm⁻¹) | 1.24 | 4.41 | 26.22 | 110.45 | 657.9 | 1774 |
3.1. Electrical properties

The electrical properties of GaSb layers doped with Si were obtained from Hall measurement at room temperature. A wide range of Hall concentration from $2.1 \times 10^{16}$ to $8.1 \times 10^{19}$ cm$^{-3}$ is obtained by varying the Si source temperature.

Use of GaAs substrates is necessary for Hall measurements since GaSb substrates were not available in semi-insulating form [12]. However, the large lattice mismatch (8%) and chemical incompatibility between GaSb and GaAs could influence the mobility and carrier concentration.

The measured of hole concentration versus growth temperature, are shown in Fig. 1.

3.1.1. Effect of the growth temperature on the density of doping

Undoped grown GaSb layers are always p type because of native lattice defect [13].

The hole concentration was observed to increase linearly as the growth temperature as shown in Fig. 1 this curve is considered as a reference for any Si doped layer deposited by MBE on a GaSb substrate (e.g. Per the fabrication of the tunnel junction for the active layer in the VECSEL ). The Hall mobility and the resistivity are also seen in Fig. 2 and 3, the hole mobility exhibits a decrease with increasing hole concentration. The resistivity decrease rapidly when the hole concentration is down of $5 \times 10^{17}$ cm$^{-3}$ and become constant up $10^{19}$ cm$^{-3}$.

3.2. Optical Properties

PL measurements at low temperature and the phothothermal deflection spectroscopy were used to determine the optical properties.

3.2.1. PL measurements

3.2.1. a. influence of temperature on the PL spectra:

Fig. 4, 5, 6, 7, 8, and 9 illustrated the evolution of the low temperature PL spectra with temperature in the 95-300 K range, for Si-doped GaSb with hole concentrations of $2.1 \times 10^{17}$ to $8.1 \times 10^{19}$ cm$^{-3}$. At 95 K the spectrum of the undoped (Fig. 4) and low doped layer (Fig. 5) exhibits two well-resolved transition at photon energies of 700 and 796 mev. The peak at 700 mev is attributed to a native acceptor ($V_{SbGaSb}$) transition. The origin of the 796 mev peak was assigned to a band to acceptor transition. The PL spectra of the heavy doped layers (Fig 6, 7, 8, 9) are dominated by one peak which is probably band to band optical transition. This peak decrease with the temperature. The PL spectra of the moderately and heavily doped samples are characterized by a broadening of the PL bands when the free carrier’s concentration increases (Fig. 8, 9). These features can be explained considering the interplay of different effects connected with heavy doping: (i) conduction-band filling, (ii) band gap narrowing due to carrier-carrier and carrier-impurity interactions and (iii) formation of band tails due to doping inhomogeneities [14]. The decrease of emission intensity with increasing temperature may be due to thermal ionization of excitonic radiative centers. The energy position and the FWHM of each peak have been determined by a quantitative fit to the experimental PL spectra using a sum of Gaussian line distribution, the dominant peaks were fit first and the additional peaks were
added as necessary. Fig 10 and 11 show the variation of the FWHM and band gap energy respectively, versus hole concentration.

We note that the FWHM is much greater and increases much more rapidly when increasing carriers’ density [15]. The broadening of FWHM can be explained as the impurity band merges with the valence band edge and it becomes a band tail at high doping concentrations. Because of this phenomenon, the optical transition between the conduction and the valence band are broadened. The $\Delta E_p$ (Fig.10) increases slowly up to $p=1 \times 10^{18}$ cm$^{-3}$ and rapidly for higher hole concentrations. From the data we have obtained an empirical relation for FWHM of Si doped GaSb at 95 K,

$$\Delta E(p)(eV) = 4.310^{-2} p^{1/3}$$  \hspace{1cm} (1)

We notice also in fig 11 that gap energy decreases with hole concentration. This band gap shrinkage could be described by three main mechanisms: free carriers exchange interactions, carrier’s interactions with potential impurity and doping-induced variations of lattice constant.
3.2.1. b. Temperature Dependence of the Energy gap

From PL spectra, we notice that while increasing temperature, the band gap energy decreases due to crystal lattice expanding and inter-atomic bonds weakness. Weaker bonds means less energy is needed to break a bond and get an electron in the conduction band. The relationship between temperature and the gap energy can be seen by the following well-known empirical formulation of Varshni [16], given by:

\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} \]  

(2)

where \( E_g(0) \) represent the extrapolated value of the band gap at 0 K, \( \alpha \) and \( \beta \) are empirical parameters and \( T \) is the measured temperature.

At high temperature, this formula is well fitted to experimental results, but it gives higher \( E_g \) values at low temperature.

Vina [17] has suggested an empirical expression of Bose-Einstein type, which could be used at low temperature experiments, given by:

\[ E_g(T) = E_g(0) - \frac{\lambda}{\exp(\theta/T) - 1} \]  

(3)

where \( \lambda \) is a constant and \( \theta \) is Debey temperature.

Figures 12, 13, 14, 15, 16 and 17 shows the curves of \( E_g \) variations vs temperature obtained from PL spectra analysis, fitted to the Varshni and Vina formulas.
The parameters $\alpha$, $\beta$, $\lambda$ and $\theta$ determined by fitting the experimental points with Eq (2) and (3), are summarized in table 2 and 3.

### Table 2: Varshni

| Sample         | Carrier concentration (cm$^{-3}$) | $E_{g0}$ (mev) | $\alpha$ ($10^{-4}$eV.K$^{-1}$) | $\beta$ (K) |
|----------------|----------------------------------|----------------|---------------------------------|-------------|
| GaSb(n.i.d)/GaAs | $2.1 \times 10^{16}$             | 808            | 3.86                            | 180         |
| GaSb(Si)/GaAs   | $4.95 \times 10^{16}$            | 806            | 3.87                            | 180         |
| GaSb(Si)/GaAs   | $3.43 \times 10^{17}$            | 805            | 4.1                             | 180         |
| GaSb(Si)/GaAs   | $2.1 \times 10^{18}$             | 793            | 5.48                            | 180         |
| GaSb(Si)/GaAs   | $2.3 \times 10^{19}$             | 791            | 4.69                            | 250         |
| GaSb(Si)/GaAs   | $8.11 \times 10^{19}$            | 779            | 3.27                            | 200         |

### Table 3: Vina

| Sample         | Carrier concentration (cm$^{-3}$) | $E_{g0}$ (mev) | $\lambda$ (mev) | $\theta$ (K) |
|----------------|----------------------------------|----------------|-----------------|--------------|
| GaSb(n.i.d)/GaAs | $2.1 \times 10^{16}$             | 804            | 77              | 232          |
| GaSb(Si)/GaAs   | $4.95 \times 10^{16}$            | 804            | 79              | 225          |
| GaSb(Si)/GaAs   | $3.43 \times 10^{17}$            | 799            | 79              | 225          |
| GaSb(Si)/GaAs   | $2.1 \times 10^{18}$             | 786            | 106             | 225          |
| GaSb(Si)/GaAs   | $2.3 \times 10^{19}$             | 782            | 73              | 240          |
| GaSb(Si)/GaAs   | $8.11 \times 10^{19}$            | 774            | 60              | 230          |

3.2.2. Photothermal measurements:
The photothermal signal measured with lock in amplifier, have two compounds: phase and amplitude that will be compared to the phase and modulus of the theoretical surface temperature $T_0$. Thus, we can determine absorption spectrum near the band gap energy as well as thermal conductivity.

3.2.2. a. Effect of doping on absorption spectrum

Figure 18 show the experimental curves of the normalized amplitude for the six samples: undoped and Si-doped GaSb epilayers with different doping levels.

![Fig18. Normalized Amplitude of photothermal signal versus wave length and Si-doped GaSb layers](image1)

![Fig19. Absorption spectra versus energy of undoped for undoped and Si-doped GaSb epilayer](image2)
The amplitude of undoped and low Si-doped GaSb with density of doping saturates for energies above the gap \( (E_g < 1.7 \, \mu m) \) because of high absorption then it decreases towards a minimum at the transparency region below the gap. In the other hand, the minimum of amplitude is much greater for heavily doped samples because of the high free carriers' contribution to the optical absorption \([18, 19]\). Therefore, we can use this minimum to determine free carriers concentration \([10]\).

The optical absorption spectrum in the band gap region is obtained while comparing the slope of the photothermal amplitude (or phase) to the corresponding theoretical one \([10]\).

The obtained spectra in Fig. 19. shows that doping increases the absorption in the transparency region \([18]\) and shifts the absorption edge to low energies (Burstein–Moss effect).

3.2.2. b. Determination of the gap energies

In order to obtain the gap energy \( E_g \) from optical spectrum, we have used the Tauc method \([20, 21]\). For excitation energies \( E = h\nu \) higher than \( E_g \), the quantity \( (\alpha E)^n \) should have linear variations with \( E \), following the Tauc law:

\[
(\alpha E)^n = \beta (E - E_g)
\]

where \( \alpha \) is the absorption coefficient and \( \beta \) is a constant, and \( n = 2 \) for direct band gap semiconductors such as GaSb.

![Graph showing \((\alpha E)^2\) versus photon energy \(E\) near the band gap of undoped and low Si-doped GaSb](image1)

![Graph showing band gap shift versus \(P^{1/3}\) for Si-doped GaSb epilayer](image2)

The curves of \( (\alpha E)^2 \) versus photon energy \( E \) obtained with the six samples are shown in figure 20. From the intersection between the curves slope for high energies and the energy axis we obtain the gap energy \( E_g \). The obtained values of \( E_g \) are reported on table 3 which is compared with PL gap energy. We notice that the gap energy of doped samples shifts toward lower energies. This bandgap shift \( -\Delta E_g \) increases with dopants density \( P \). Moreover, curves in Fig. 21 show that \( -\Delta E_g \) varies linearly with \( P^{1/3} \), so we can write: \( -\Delta E_g = k_1 \cdot P^{1/3} \) where \( k_1 = -0.88 \times 10^{-8} \). This relation can be used to determine the doping density.

In table 4, the gap energies measured with PL spectra and photothermal deflection has been compared for different doping levels. We notice that the \( E_g \) (PL) is slightly higher than the real gap energy determined by photothermal deflection, because it corresponds to the radiative transition.

| Hole concentration (cm\(^{-3}\)) | \( E \) (PL) | \( E_g \) (Photothermal deflection spectroscopy) |
|-------------------------------|-------------|----------------------------------|
| \( 2.1 \times 10^{16} \) | 0.73752 | 0.727 |
| \( 4.95 \times 10^{16} \) | 0.73617 | 0.726 |
| \( 3.43 \times 10^{17} \) | 0.72984 | 0.718 |
| \( 2 \times 10^{18} \) | 0.7233 | 0.7062 |
| \( 2.3 \times 10^{19} \) | 0.71662 | 0.699 |
| \( 8.1 \times 10^{19} \) | 0.71388 | 0.692 |
3.2.2.c. Thermal conductivity:

Near the gap, the photothermal signal phase saturates in both high and low absorption regions. In the case of a thin layer semiconductor, the phase difference between the two saturations closely depends on its thermal conductivity. The thermal conductivity values obtained while comparing experimental phase difference (Fig. 22) to the corresponding theoretical value are reported on table 5.

![Fig. 22. Photothermal phase versus wavelength for undoped and Si-doped GaSb layers](image)

Table 5. Thermal conductivity vs hole concentration of undoped and Si-doped GaSb layers

| Sample                   | Thermique Conductivity (W m\(^{-1}\) K\(^{-1}\)) |
|-------------------------|-----------------------------------------------|
| GaSb (n1d)/GaAs         | 0.315                                         |
| GaSb (700°C)/GaAs       | 0.22                                          |
| GaSb (1080°C)/GaAs      | 0.4                                           |
| GaSb (1150°C)/GaAs      | 0.236                                         |
| GaSb (1250°C)/GaAs      | 0.42                                          |
| GaSb (1300°C)/GaAs      | 1                                             |

We remark that the conductivity is very low because of the large lattice mismatch (8%) and chemical incompatibility between GaSb layer and GaAs substrate, leading to a reduction of the free mean path of phonons, which increases the interface thermal resistivity. However, for heavily doped samples we notice a thermal conductivity increase that is due to the additional free carriers.

4. Conclusion

Silicon doped GaSb have been investigated for the influence of both temperature and hole concentration on the optical and electronic properties, using Hall effect measurements, photothermal deflection spectroscopy and low temperature photoluminescence spectroscopy.

The Hall Effect data shows a monotonic increase in hole concentration from \(2.1 \times 10^{16}\) to \(8.1 \times 10^{19}\) cm\(^{-3}\) with increasing growth temperature. Furthermore, PL spectra dramatically broadened with increasing doping concentration, suggesting the onset of impurity banding.
Moreover, the temperature dependence of the PL implies a banding energy of the radiative centres, presumed to involve silicon. From the energy position of the PL peak for these highly doped samples it was also possible to make an estimation of the free hole density. This procedure takes into account the band filling and band-gap shrinkage effects. Finally, we have investigated the optical absorption changes induced by doping for silicon doped GaSb samples by photothermal deflection spectroscopy, we show that the absorption edge shifts towards low energies. We also notice that thermal conductivity is very low due to thermal resistivity of the layer-substrate interface.

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