

# Optical characterization of Te-doped $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$ epitaxial layers grown by liquid phase epitaxy

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A set of  $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{Sb}_{1-y}$  quaternary layers were grown on (100) GaSb substrates using the liquid phase epitaxy technique (LPE). These layers were doped with tellurium and were characterized by Raman, Photoluminescence (PL) spectroscopy, and Secondary Ion Mass Spectroscopy (SIMS). Several optical modes were identified by performing Raman spectroscopy characterization at room temperature and observing the effect of the impurity concentration on the Raman mode frequencies. From secondary ion mass spectrometry the concentrations of Te in the liquid solutions and the electron densities present in the layers were obtained. Finally, these last results were compared with those obtained from low temperature photoluminescence spectroscopy measurements at low temperatures on this set of samples.

*Keywords:* III-V semiconductors; Liquid Phase Epitaxy

## 1. Introduction

Antimony-based III-V compound semiconductors such as GaInSb, AlGaAsSb, GaInAsSb and InAsPSb have been studied because they are the basis for the development of optoelectronic devices such as photodiodes, lasers, photodetectors, solar cells, thermophotovoltaic cells, etc., which perform in the infrared medium range [1-5]. These devices are being employed in areas such as medicine, environmental monitoring, and optical communications, among others [6-7].

In particular, the band gap energy of the GaInAsSb quaternary alloys can be tuned in the range between 1.7 to 2.3  $\mu\text{m}$ , and it is possible to obtain them with a good crystalline lattice match between layer and substrate using either GaSb, InP or InAs substrates. These types of layers have been grown using technique such as Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapor Deposition (MOCVD), and Liquid Phase Epitaxy (LPE) techniques [8-11]. However, the growth of these semiconductor alloys is complicated because a broad

immiscibility region is present for this type of alloy [8, 9].

Using the liquid phase epitaxy technique, it has been possible to grow these GaInAsSb layers with a high degree of crystalline quality [12]. To get this, it is fundamental that the growth parameters involved in the growth process, such as growth temperature ( $T_c$ ), supercooling temperature ( $T_{sc}$ ), and cooling rate ( $r_c$ ), must be optimized in order to get epitaxial layers with a high degree of crystalline quality and a lattice mismatch with the GaSb substrate as small as possible.

In this work we describe the characterization done in a series of Te-doped GaInAsSb quaternary layers grown on GaSb substrates by LPE with different Te concentrations. From this characterization we were able to obtain the layer stoichiometry, the density of Te doping in each layer, and the effect of the doping on the sample crystalline quality.

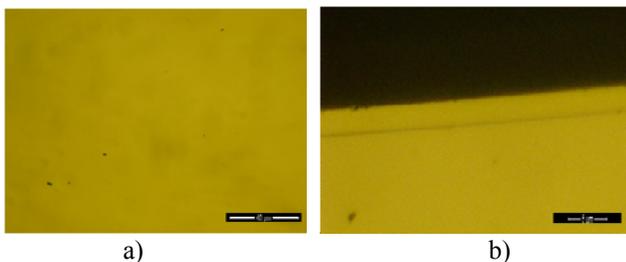


Figure 1. Microphotographs showing the surface and the substrate-layer interface of a GaInAsSb layer grown on a GaSb substrate.

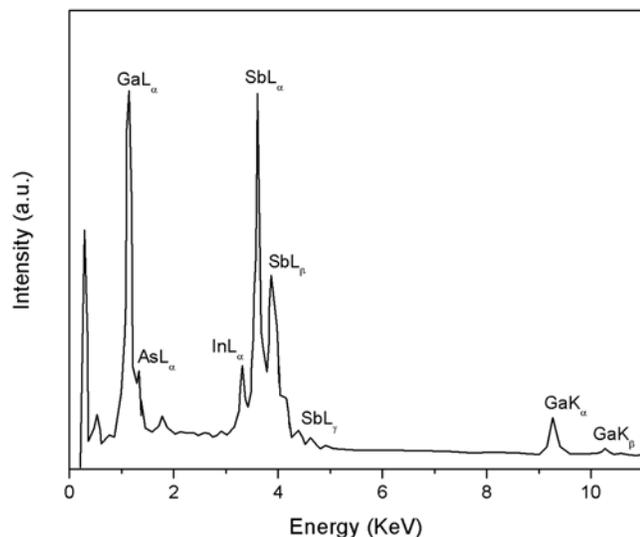


Figure 2. SEM-EDX spectrum for a GaInAsSb layer.

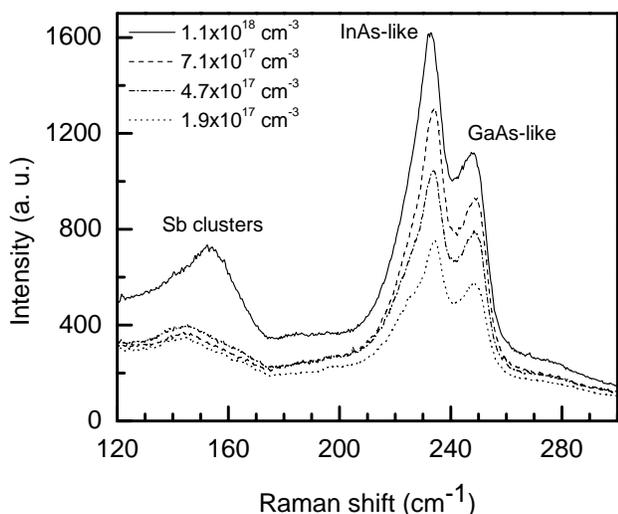


Figure 3. Room temperature Raman spectra for the Ga<sub>0.85</sub>In<sub>0.15</sub>As<sub>0.15</sub>Sb<sub>0.85</sub> layers with different Te concentrations.

## 2. Experimental Details

Quaternary GaInAsSb epitaxial layers were grown in a three-zone furnace in a H<sub>2</sub>-atmosphere, using a horizontal graphite sliding boat. As substrates, (100) GaSb wafers mechanically polished from Firebird, Inc. were used. All the precursors elements used to prepare the growth melt were of 6N purity, and GaAs came from a wafer. For the intentional doping of the GaInAsSb epitaxial layers, small quantities of the Sb<sub>3</sub>Te<sub>2</sub> alloy were added to the growth solution.

After the charge of the substrate in the boat, the temperature was raised at 640°C for one hour, in order to eliminate the oxide in the substrate surface. Then, the temperature was decreased to stabilize the system, and a cooling ramp at a rate of about 0.3 °C/min was established, after which the layers were grown at temperatures around 530 °C.

Elemental chemical microanalysis measurements were performed using a scanning electron microscope (SEM) FEI-Quanta 3D FEG model equipped with a X-ray dispersive energy microanalysis system (EDX). High resolution X-ray diffraction (RXHR) measurements were performed in the quaternary layers using a Panalytical XPERY MRD model. The atomic concentration of the dopant, Te, was determined by using a secondary ion mass spectrometer (SIMS) from CAMECA, model ims 6f, with a Cs primary ion beam. Raman spectra were recorded at room temperature using the 6328 Å line of a He-Ne laser as the exciting source. Photoluminescence (PL) measurements were done at a temperature of 15 K, using the 488 nm line of an Ar<sup>+</sup> laser as the exciting source.

## 3. Results and discussions

Sample thickness was determined using an optical microscope on the layers previously treated with an etching to reveal the interface substrate-layer; in all cases, the layer average thickness was around 3 microns. In Figure 1 it can be observed the microphotographs of the layer surface, as well as the substrate-layer interface.

In Figure 2 it is shown an EDX image showing the composition for one of the quaternary layers; we found only the elements present in the precursor elements. From EDX characterization it was determined that the stoichiometry of the quaternary layers. For all the samples we obtained: Ga<sub>0.85</sub>In<sub>0.15</sub>Sb<sub>0.85</sub>.

From the results obtained in the RXHR measurements it was obtained that the lattice mismatch between substrate and layer, ( $\Delta a/a$ ), was in the order of 4.5 x 10<sup>-4</sup> for all samples.

In order of incorporate different concentration of Te atoms on the samples, small quantities of Sb<sub>3</sub>Te<sub>2</sub> were added to the growth solution. Secondary Ion Mass Spectroscopy were used for determinate the Te concentration in each sample. In Table 1, we presented the concentration of the Te atoms, for each Sb<sub>3</sub>Te<sub>2</sub> percentage in the growth solution. We found a monotony

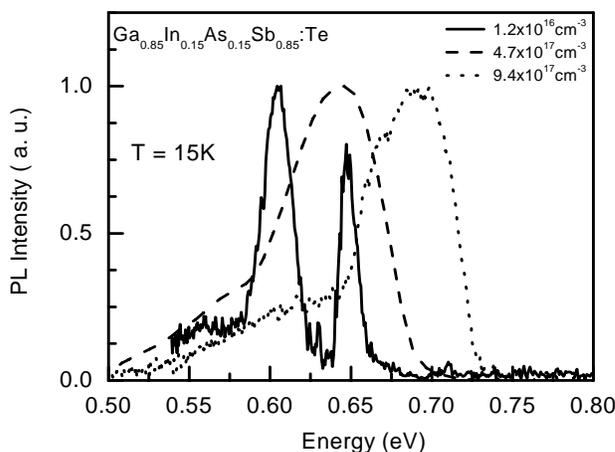
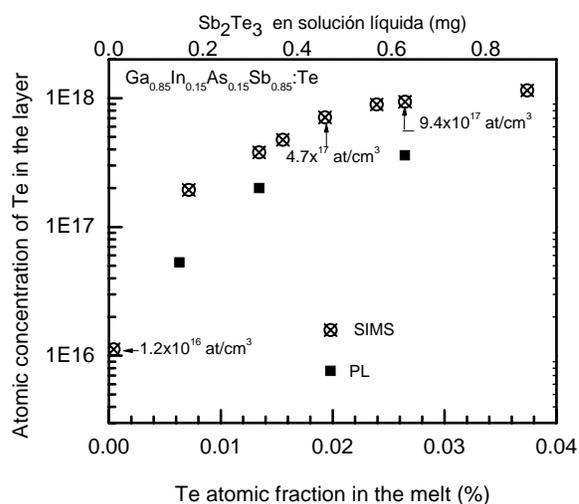
**Table 1.** Quantities of  $\text{Sb}_3\text{Te}_2$  added to the  $\text{GaInAsSb}$  layers.

$\text{Sb}_3\text{Te}_2$ (%)	cc. of Te ( $\text{at}/\text{cm}^3$ )
0.00042	$1.2 \times 10^{16}$
0.00714	$1.9 \times 10^{17}$
0.01344	$3.8 \times 10^{17}$
0.01554	$4.7 \times 10^{17}$
0.01932	$7.1 \times 10^{17}$
0.02394	$8.9 \times 10^{17}$
0.02646	$9.4 \times 10^{17}$
0.03738	$1.1 \times 10^{18}$

increase if the Te atoms with respect the increase of %  $\text{Sb}_3\text{Te}_2$ .

In Figure 3 it is shown the room temperature Raman spectra of the Te-doped  $\text{Ga}_{0.85}\text{In}_{0.15}\text{As}_{0.15}\text{Sb}_{0.85}$  at different Te concentrations. It can be observed the presence of three peaks at Raman frequencies of  $235\text{cm}^{-1}$ ,  $249\text{cm}^{-1}$  and a broad band peaked between  $145$  and  $155\text{cm}^{-1}$ . The first two are due to the InAs-like LO mode, and the GaAs-like LO mode [13]; and the last one can be correlated to the presence of free carriers due to the presence of Sb clusters [14]. The slight shoulder observed at the low frequency side of the InAs-like band is attributed to InSb-like LO modes [13].

The normalized photoluminescence (PL) spectra for the three Te-doped  $\text{GaInAsSb}$  epitaxial layers are shown in Figure 4. For the sample with a Te concentration of  $1.2 \times 10^{16}\text{cm}^{-3}$ , there is a free electro-to-acceptor transition centered at about  $614\text{meV}$ , which is dominant in the PL spectrum; and another PL band peaked at around  $653\text{meV}$  due to a bounded-exciton recombination. For the  $\text{GaInAsSb}$  sample doped with a Te concentration of  $4.7 \times 10^{17}\text{cm}^{-3}$  there appears a PL broad band centered at about  $646\text{meV}$  due to the high concentration of carriers. For the highest Te-doped sample, with a Te concentration of  $9.4 \times 10^{17}$ , we observe a broad PL band shifted to higher energies peaked around  $689\text{meV}$ , which shifts to higher energies because of a band-filling effect [15]. A shift to higher energies of the PL band is observed as the Te concentration in the quaternary layers increases. In Figure 5 are shown the Te liquid atomic fraction obtained from the SIMS measurements, as a function of the Te concentration in the  $\text{GaInAsSb}$  layers. The filled square symbols correspond to the data obtained from the PL measurements adjusted to the band-filling model [16]. The electron concentration measured through the low temperature PL spectra and fitting the PL peak with the band-filling model, which takes into account the shift of the Fermi energy towards the conduction band as the donor concentration increases, shown a good agreement with the results obtained with the SIMS measurement. These results suggest that the Te atoms incorporated to the samples was electron donors.

**Figure 4.** PL spectra for the Te-doped  $\text{GaInAsSb}$  epitaxial layers with different Te concentration.**Figure 5.** Te liquid atomic fraction as a function of the atomic Te concentration in the quaternary  $\text{Ga}_{0.85}\text{In}_{0.15}\text{As}_{0.15}\text{Sb}_{0.85}:\text{Te}$  epitaxial layers.

#### 4. Conclusions

High crystalline quality  $\text{GaInAsSb}:\text{Te}$  epitaxial layers were grown on (100)  $\text{GaSb}$  substrates by the LPE technique. Several growth parameters were varied in order to optimize the quality of the layers and the quality of the substrate-layer interface in such a way as to obtain the lowest values possible of the lattice mismatch parameter.

Using SIMS measurements it was possible to obtain the concentration of the Te dopant used to control the electrical conductivity of the samples. These SIMS results were compared to the electron concentration measured through the low temperature PL spectra and fitting the PL peak energy with the band-filling model which takes into account the shift of the Fermi energy towards the conduction band as the donor concentration increases. A shift to higher energies of the PL band is observed as the Te concentration in the quaternary layers increases. A good agreement was obtained from the comparison of the results from SIMS and PL.

Room temperature Raman spectra showed the presence of two bands coming from the InAs-like LO Phonon with higher intensity, and from the GaAs-like LO phonon.

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