Identification of the additional transition around the $E_0$ critical point in photoreflectance spectra of GaInAsSb epitaxial films

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Abstract. We present the analysis of the photoreflectance (PR) spectra line-shape of GaInAsSb films over GaSb. The studied samples were grown by liquid phase epitaxy technique. The growth parameters such as initial temperature and contact time were the same for all samples, but the precursor solution varied slightly in the As concentration. The cooling rate was different for each sample. The PR spectra were obtained at low temperature, modulated by a 632.8 nm He-Ne laser. These spectra were fitted using the third derivative lorentzian function but, for one of the samples exhibiting an additional structure around the $E_0$ critical point oscillation, it was also necessary to use a first derivative lorentzian function, associated to an excitonic transition. This interpretation of the new PR feature was analyzed according to X-ray diffractograms. Comparing the FWHM of the main peak in the diffractograms it was found that the sample which exhibits the excitonic transition has the best crystalline quality, and was the sample with the lower cooling rate. The excitonic energy value obtained (9.7 meV) is in agreement with the value reported in the related literature.

1. Introduction

GaInAsSb alloys are semiconductor materials with interesting applications on optoelectronic devices such as thermophotovoltaic cells, lasers, and detectors in the infrared range [1,2]. Liquid phase epitaxy (LPE) layers of Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ grown over GaSb and InAs substrates had been reported [3,4]. The selection of the substrate is according to the chosen $x$ and $y$ values. For layers with low $x$ and $y$ values the appropriate substrate is GaSb in order to obtain a good lattice match. In this type of quaternary alloys, properties such as the values of the energy band gap $E_0$ and lattice constant $a$ may be tailored to the desirable performance spectral range by controlling the molar fraction of the constituent elements ($x$ and $y$) [5-9]. In this work we studied by means of photoreflectance and X-ray diffraction, Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ layers grown by liquid phase epitaxy over GaSb substrates. The films are GaSb-rich. LPE growth technique is based in a slightly difference from the thermodynamic equilibrium between the solid (substrate) and the liquid solution, inducing the solid phase over the substrate by lowering the liquid solution temperature to saturate or supersaturate it. As the temperature decreases, the solid phase over the substrate appears and the molar fractions of the constituent elements in the liquid solution change due to the difference between its diffusion coefficients. And so the stoichiometry of the grown layer and its lattice parameter depend on the cooling rate and the initial and final growth
temperature. For material systems where it can be used, LPE has the advantage of yielding layers of accurately controlled composition and thickness, since only a few growth parameters can be varied, i.e., substrate orientation, liquid solution composition, temperature, cooling rate, and growth time [10]. The optical response of these layers is strongly related to growth parameters.

Although it is of great interest to understand the optical properties of this alloy [11,12], only a few photoreflectance (PR) measurements have been reported in the literature [13]. This is a modulated reflectivity technique in which the surface electric field of the sample is modulated by an incident chopped electromagnetic radiation. Variations on the intrinsic field produce modifications on the electronic band structure and so, in the reflectivity of the sample.

Based on the line shape, line width and energy of oscillations in the PR spectra it is possible to obtained energy values associated to electronic band structure critical points (CP’s), identification of excitons, and information about electron-phonon interactions. The PR line shape is strongly related to the type of critical point. Considering the symmetry of the CP’s in the band structure, it is possible to define one, two or three dimensional critical point, if the number of effective masses equal to infinite is two, one or none, respectively. In the low field regime, the PR spectra features of the different CP’s could be described by Aspnes expression [14], varying some parameters according to the type of CP. We used this basic characteristic of the PR technique to identify the type of CP and the electronic transition associated to it. Muñoz et al. [13] present the analysis of the $E_0$ critical point and its behavior with temperature, but in this work we studied the additional structure present on the PR spectra and the identification of the type of critical point associated. These results are correlated with cooling rate and with crystalline quality of the samples, studied by means of X-ray diffraction patterns.

2. Experimental Procedures

The three samples under study were grown by LPE over GaSb (100) substrates by precursor quaternary liquid solutions In-rich. The solid solutions obtained have a high content of Ga and Sb. The LPE used is a conventional system with a horizontal graphite boat and a three zone furnace. The growth atmosphere was purified hydrogen from a Pt-Ag diffusion cell. The epitaxial layers, named S1, S2 and S3, were grown at 530 °C with the growth parameters presented in table 1.

| SAMPLE | S1         | S2         | S3         |
|--------|------------|------------|------------|
| $X_{Ga}$ (%) | 18.544     | 18.541     | 18.542     |
| $X_{In}$ (%)  | 57.833     | 57.835     | 57.825     |
| $X_{As}$ (%)  | 0.147      | 0.147      | 0.162      |
| $X_{Sb}$ (%)  | 23.476     | 23.477     | 23.471     |
| Cooling rate (°C/min) | 0.144 | 0.083 | 0.288 |
| t (min)       | 4:51       | 4:50       | 4:30       |

The optical characterization was accomplished by photoreflectance technique at low temperature, with a He-Ne laser as modulating beam. The light probe used was the output of a monochromator with 32 cm of focal distance, and a 120 W QTH lamp beam. The samples holder was in a He close cycle cryostat, and the measurements were done at 12 K, with a thermoelectrically cooled PbS detector. For the structural characterization, X-ray diffraction patterns were used in the low incident angle configuration. They were recorded with a Bruker D8 Advance diffractometer, using Cu $K_α$ radiation, and a graphite monochromator with the detector. The measurement mode was a detector scan for low incident angles. Considering that the samples are epitaxial layers, the main response in this
measurement configuration is due to the film instead of the substrate. For each chosen incident angle the diffraction patterns exhibited a very few peaks mostly at high 2θ values.

3. Results and Discussion

The photoreflectance spectra at 12 K are presented in figure 1. In all of them there is a main oscillation, attributed to the $E_0$ critical point, corresponding to the band gap energy. A second oscillation is observed in samples S2 and S3, at lower energy. This last feature was studied using the first derivative lorentzian function, associated to excitonic transitions. The spectra were fitted using two contributions, for S2 and S3 samples, and just one contribution for S1 fitting [14]. For all samples the PR spectra were fitted with the following expression [15]:

$$\frac{\Delta R}{R} = \Re \left\{ C_1 e^{i\theta} \left( E - E_{CP1} - i\Gamma_1 \right)^{-2} + C_2 e^{i\theta} \left( E - E_{CP2} - i\Gamma_2 \right)^{-2.5} \right\}$$

in which $C_1$ and $C_2$ are the amplitude of each oscillation, $E_{CPi}$ is the critical point energy, i.e. transition energy, $\Gamma$ is the phenomenological broadening parameter, and $\theta$ is the phase. The first term of the right part of the equation (1) is associated to excitonic transitions, and the other term is associated to band to band transitions. The fitting curves observed in figure 1 were obtained using equation (1) with $C_1=0$ for S1 sample. This means that the transition responsible for the PR spectra of sample S1 is well described by a band to band critical point; instead, for samples S2 and S3 it was necessary to add a contribution ($C_1 \neq 0$) corresponding to an excitonic transition. This is the expected optical response of a high crystalline quality material. The excitonic binding energy obtained for S2 was 9.7 meV; this value is in the order of the reported value for GaSb [16].

**Figure 1.** PR spectra at low temperature of GaInAsSb samples grown over GaSb substrates.

**Figure 2.** X ray diffraction pattern for low incident angle, of GaInAsSb samples grown over GaSb substrates.
For some semiconductor materials, PR spectrum features in the vicinity of the band to band transition have been reported. These features are associated to the line shape of a 1D critical point [17]. Equation (1) is still valid for excitonic transitions considering they form a discontinuous parabolic band, as was argue by Batz [18].

The diffraction patterns obtained in the low incident angle configuration are presented in figure 2. As the measurement mode is of low penetration depth, these patterns have exclusively film contribution, without contribution of the substrate. In the 2θ range chosen, the PDF of GaSb exhibit a diffraction maximum in 76.514° due to the (422) planes. Even though samples S2 and S3 patterns present diffraction at angles lower than GaSb, the FWHM of the peaks is small compared to the S1 pattern. This result is coherent with the optical response obtained due to the existing relation between FWHM and crystalline quality. In the other hand, the angle shift of the peak in S2 and S3 patterns is attributed to the inclusion of In and As in the GaSb matrix, changing the lattice parameter. Calculating the differences between the lattice parameters of sample S2 and GaSb substrate, the lattice mismatch is 4.5 x 10^{-3}. This value means that there is some distortion of the unit cell, increasing toward the generation of misfit dislocations. Instead, diffraction pattern of sample S1 has several peaks not resolved. It is possible that sample S1 has a low crystalline quality and possible present of other phases. The different optical and structural response of samples under study could be explained as a consequence of growth parameters such as cooling rate and relative molar fractions in the liquid solution. S2 is the most homogeneous and crystal.

4. Conclusions
The line shape of PR spectra contains important information about the critical points involved in the optical transitions on the semiconductor layers. The GaInAsSb samples fabricated by LPE showed differences in the optical response, influenced by the growth parameters. The analysis of X-rays and PR measurements evidenced excitonic effects on samples S2 and S3 attributed to growth conditions. Experimental results can be interpreted as a good crystalline quality of quaternary samples S2 and S3, while S1 sample exhibited a possible presence of other phases. The lattice mismatch value of S2 sample, 4 x 10^{-3}, which could generate a low dislocation density. The excitonic binding energy evaluated from PR measurements on S2 sample is 9.7 meV.

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