Lattice vibrations study of Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ quaternary alloys with low (In, As) content grown by liquid phase epitaxy

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Abstract. Raman scattering spectroscopy was used to measure and analyze the lattice vibrations in some quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloys with low (In, As) contents, (0.03 < x < 0.12 and 0.03 < y < 0.10). The layers were grown by liquid phase epitaxy on (001) GaSb substrates at 540 °C. High Resolution X-Ray Diffraction results showed profiles associated with a quaternary layer lattice matched to the GaSb substrate as obtained from the (004) reflection. The experimental diffractograms were simulated to estimate alloy composition, thickness and lattice mismatch of the layer. Raman scattering results show phonon frequencies associated to the TO and LO GaAs-like modes as well as GaSb+InAs-like mode, which are characteristic of this quaternary alloy. The As content dependence of the phonon frequency measured in this alloy for low (In, As) contents agree well with the modified Random-Element Isodisplacement (REI) model and also with other available experimental reports. This method can also be used to estimate alloy compositions for this kind of quaternary alloys.

1. Introduction

The quaternary GaInAsSb alloy lattice matched to GaSb is a narrow band-gap semiconductor (0.3-0.7 eV) with a number of applications including thermophotovoltaic cells [1], infrared light-emitting diodes [2] lasers [3] and photodetectors [4]. The growth of this alloy, however, is fundamentally difficult because of the existence of a large miscibility gap [5]. Metastable alloys have a tendency to decompose into regions with non-uniform alloy composition which is undesirable due to the degradation of the structural [6], optical [7] and electrical [8] properties. The growth of GaInAsSb alloys by LPE Liquid Phase Epitaxy) [9], MOCVD (Metalorganic Chemical Vapor Deposition) [10], MBE (Molecular Beam Epitaxy) [11], and LPEE (Liquid Phase Electroepitaxy) [12], has been reported. For this reason it is important to know about the structural properties of this kind of quaternary alloy. Only a few number of papers report studies on the vibrational properties of GaInAsSb [13, 14, 15] which give important information on some structural properties of this system. Kleinert [13] reported theoretical studies of infrared absorption spectra of GaInAsSb by using the mean-field approximation. Jaw et. al. [14] applied a modified random-element (REI) model developed by them to calculate the frequency shift of the TO and LO modes of GaAs, GaSb, InAs and InSb lattice vibrations in the quaternary alloy. More recently Vorlícek et. al. [15] reported vibrational properties of GaInAsSb grown on GaSb by LPE using the Raman scattering technique for an As content between 0.13 and 0.26. In this work, the optical lattice vibrations for low (In, As) content in Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloys (0.03 < x < 0.12 and 0.03 < y < 0.10) grown on (001) GaSb substrates by liquid
phase epitaxy are studied. Phonon frequencies of the lattice vibrations were analyzed using Raman scattering techniques. The agreement between the composition dependence of the phonon frequency with the available theoretical and experimental information is discussed.

2. Experimental procedure

Quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ solid solutions were grown by the horizontal graphite slide conventional technique for Liquid Phase Epitaxy (LPE) on n-type (001) orientation GaSb:Te substrates. A flux of pure hydrogen from a Mr. Hydrogen Purifier System, at atmospheric pressure, was used for the experiments. Dew point temperatures around -96 °C in normal growth runs, were observed. Melting was accomplished using 7N Ga, 6N In, 6N Sb and undoped GaAs as an arsenic source. We obtained the values 0.6126, 0.1188, 8.82x10$^{-4}$ and 0.2677 for the $x_l$ In, $x_l$ Ga, $x_l$ As and $x_l$ Sb atomic fractions, respectively, from the Panish and Jordan model [16]. The saturation temperature was found by visual observation and it is in good agreement with the theoretical temperature used (540 °C). Raman scattering experiments were performed at room temperature using the 5145 Å line of an Ar laser at normal incidence for excitation. The laser power used in these measurements was 20 mW. Care was taken in order no to heat the sample to avoid heat induced crystallization during Raman measurements. Scattered light was analyzed using a Jobin-Yvon T64000 triple spectrometer, operating in the subtractive configuration, and a multichannel charge-coupled device detector cooled at 140 K using liquid nitrogen. Typical spectrum acquisition times were limited to 60 sec to minimize the sample heating effects mentioned above. High Resolution X-Ray Diffraction (HRXRD) measurements were made using a Bartels monochromator in the Ge (022) reflection mode, with a Cu anode as the source of x-ray radiation. The x-ray source was operated at 30 kV and 30 mA. Diffraction profiles were obtained from the (004) reflection.

3. Results and discussion

Figure 1 shows a typical HRXRD rocking curve measured for the quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloy. Two prominent peaks associated to the GaSb substrate and to the quaternary layer are observed. The experimental curve is represented with a dotted line whereas the simulated curve is shown as a continuous line. Such simulation was performed using the Takagi-Taupin theory [17] which provides an estimate of the thickness, alloy composition ($x, y$) and lattice mismatch of the quaternary layers. In Table 1 the obtained data are enlisted. The lattice mismatch value estimated suggests relaxed layers with a good crystalline quality. In Fig. 2 are depicted Raman scattering spectra of Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ layers for three different alloy compositions ($x, y$). The observed bands were deconvoluted using three Lorenztian curves and the fits are plotted using a continuous line. Two intense peaks are identified and
Table 1. Composition, layer thickness and lattice mismatch obtained from the simulation of experimental HRXRD rocking curves for the Ga$_{1-y}$In$_y$As$_x$Sb$_{1-x}$ alloy. The phonon frequencies of the lattice vibrations measured by Raman scattering are also shown.

| HRXRD composition | Layer thickness ($\mu$m) | Lattice mismatch | Raman phonon frequency (cm$^{-1}$) |
|-------------------|--------------------------|-----------------|----------------------------------|
| In ($x$) As ($y$) |                          |                | GaSb+InAs TO LO GaAs |
| 0.03 0.03         | 2.50                     | 2.99x10$^{-4}$  | 225.1 240.9                     |
| 0.07 0.07         | 0.45                     | 1.84x10$^{-3}$  | 228.1 243.7                     |
| 0.12 0.10         | 2.00                     | 8.00x10$^{-4}$  | 228.5 243.2                     |

associated to the LO GaAs-like mode (high frequency peak) and a mixed GaSb+InAs mode (low frequency peak). Also, a broad band near 217 cm$^{-1}$ can be associated to the TO InAs-like lattice vibration [18]. The presence of a mixed GaSb+InAs mode is due to the proximity in frequency position of these lattice vibrations. Both the LO GaAs-like and the mixed GaSb+InAs modes shift to high frequencies as the As content increases. No InSb mode has been observed in the spectra. In addition we see no scattering due to compositional clustering or phase segregation.

Fig. 2. Experimental and deconvoluted Raman spectra of Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ layers grown on GaSb substrates for several low compositions $x, y$.

Fig. 3. Dependence of the phonon frequency of the lattice vibrations in Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ layers as a function of the As content.

The variation in optical phonon frequency of the LO GaAs-like and mixed GaSb+InAs modes is plotted in Fig. 3 as a function of the As content, $y$, in the quaternary alloy. In the same figure are also presented with symbols the experimental phonon frequencies reported in other works [13,14,15] for the same alloys at different compositions and substrates. The results of this work are denoted by half-colored squares. The continuous line represents the variation of the phonon frequency of the LO and the TO GaAs-like modes and also that of the mixed GaSb+InAs-like mode as a function of the As content. These curves were reported by Jaw et. al. [14] and were calculated using a modified random-element isodisplacement (REI) model. From the results presented in this work for low In and As composition values, it is observed a good agreement between the experimental phonon frequencies obtained by Raman measurements and the modified REI model. In the same Fig. 3 the dashed line shows a similar behavior observed in the ternary GaAs$_x$Sb$_{1-x}$ alloy reported by McGlinn et. al. [19]. In
such ternary alloy it is observed the classic two-mode behavior for the optical phonons throughout the concentration range exhibited. The different frequency shifts show a noticeable LO-TO splitting of the GaAs-like mode as the As contents increase, and a LO-TO splitting of the GaSb like mode as the As content decreases. However for the quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloy the LO-TO splitting of GaAs like mode starts near 240 cm$^{-1}$, whereas the LO-TO splitting of the resting GaSb+InAs-like mode seems to start near 228 cm$^{-1}$ with y=0.35. In this form we have characterized by Raman scattering the phonon frequencies of the lattice vibrations in the quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloy for low (In, As) contents (0.03 <x< 0.12 and 0.03 <y< 0.10). The experimental results are in good agreement with available theoretical and experimental reports. This method can be used, among other purposes, to estimate alloy compositions of this kind of quaternary alloys.

4. Conclusions

We have measured and analyzed the phonon frequency of the lattice vibrations in the quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ alloy for low (In, As) contents, (0.03 <x< 0.12 and 0.03 <y< 0.10). HRXRD results showed diffraction profiles associated to a quaternary layer lattice matched to a GaSb substrate, obtained from the (004) reflection. The experimental diffractograms were simulated to estimate alloy composition, thickness and lattice mismatch of the layer to be associated with lattice vibrations. Raman scattering results show phonon frequencies associated with the TO and LO GaAs-like modes as well as the TO GaSb+InAs-like mode, which are characteristic of this quaternary alloy. The As content dependence of the phonon frequency measured in this alloy agree well with the modified random-element isodisplacement (REI) model and also with available experimental reports. This method can be used, among other purposes, to estimate alloy compositions of this kind of quaternary alloy.

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