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Morphological studies of annealed GaAs and GaSb surfaces by micro-Raman spectroscopy and EDX microanalysis

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Abstract

Electron diffraction X-ray (EDX) microanalysis and micro-Raman spectroscopy were used to study the annealed semiconductor surfaces. EDX images showed evidences of two types of regions on the annealed GaAs and GaSb surfaces. Micro-Raman results displayed good proof of two different regions into the surface of both semiconductors, since the spectra of one region showed considerable differences to the spectra of the other. The most notable difference is the transverse optical (TO) activation and the decrease of intensity of other Raman lines in the spectra of very small regions. This work calls attention to the sensibility of micro-Raman experiments to short-length defects, which cannot be detected by EDX analysis.

Keywords: Surface structure; Morphology; Roughness; Topography; Raman scattering; Scanning electron microscopy (SEM); Gallium arsenide; Gallium antimonide

1. Introduction

The study of annealed semiconductor surfaces is very important because the structural and chemical damages influence the transport properties and as a consequence, the devices performance. For example, in the case of implanted samples the carrier distribution profile is influenced by the formation of clusters and defects. Electron microscopies have been used to study the morphology of these surfaces and the structure of As clusters in As-implanted GaAs [1]. These studies contribute to the characterization of processes that can lead to the formation of well-controlled high density of As precipitates in a GaAs crystal. Raman studies of annealed GaAs showed the presence of crystalline As into the sample surface [2]. Similar cases of the detection of crystalline V element in oxidized III–V semiconductors have also been reported [3].

Raman analysis of micrometric small superficial regions of III–V semiconductors after either thermal or chemical treatments can be carried out using an optical microscope coupled to a Raman system. This technique, together with electron microscopies, makes possible to perform morphological studies of the sample surfaces. Recent research work using micro-Raman spectroscopy to study superficial damages in liquid encapsulated Czochralski (LEC) GaAs samples has shown little evidence of the formation of As precipitates [4], but Toufella et al. [5] showed to be possible to estimate the diameter of As clusters in

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annealed LT-GaAs. On the other hand, etching treatments of GaAs samples followed by micro-Raman measurements have demonstrated the oxidation of As (As_2O_3) on the surface of the samples [6]. Well-defined Raman lines of As_2O_3 have been detected in the spectra of etched GaAs samples, although the characteristic signals of amorphous and crystalline As have not been observed.

This paper presents a micro-Raman and electron diffraction X-ray (EDX) microanalyses results of annealed GaAs and GaSb samples. These techniques allowed characterizing the superficial morphology of the samples at different annealing temperatures. Based on an analysis of scan electron microscopy (SEM) micrographs, two distinct regions were observed in both materials. The analysis of micro-Raman spectra corroborates this interpretation, since two different spectra were obtained from these two regions.

2. Experimental details

Semi-insulating GaAs and GaSb-[0 0 1] oriented single crystal samples (MCP Wafer Technology Limited) were annealed in a conventional furnace with a flow of dry nitrogen gas to avoid oxidation. The GaAs samples were annealed at 500, 550, 600, 650, 700 and 750 °C for 30 min, while the GaSb samples were annealed at 350, 400 and 450 °C for 15 min. These temperatures are currently used in thermal treatments for these materials and the times were selected to maximize the thermal effects.

The Raman measurements were performed with a T64000 Jobin-Yvon triple monochromator coupled to an optical microscope, a cooled CCD detector and a conventional photon counting system. The 488.0 nm line of an argon ion laser was used as exciting light, always in backscattering geometry. The output power of the laser was kept within 2–5 mW to avoid overheating of the samples. All measurements were taken at room temperature.

The areas covered by micro-Raman analyses are circular and their diameter is approximately 2 μm. The penetration depth of the light is determined by the wavelength of the exciting light. For the 488 nm line of the argon ion laser, the depth probed is about 40 nm into the sample surface for GaAs and about 8 nm for GaSb [7].

The annealed samples were subjected to EDX microanalysis in an XL30FEG Phillips scanning electronic microscope coupled to an ISIS Link microanalyser (operating with a beam energy of 20 kV).

3. Results and discussions

3.1. GaAs

Fig. 1 presents the micrographs of three representative annealed GaAs samples. Two different regions

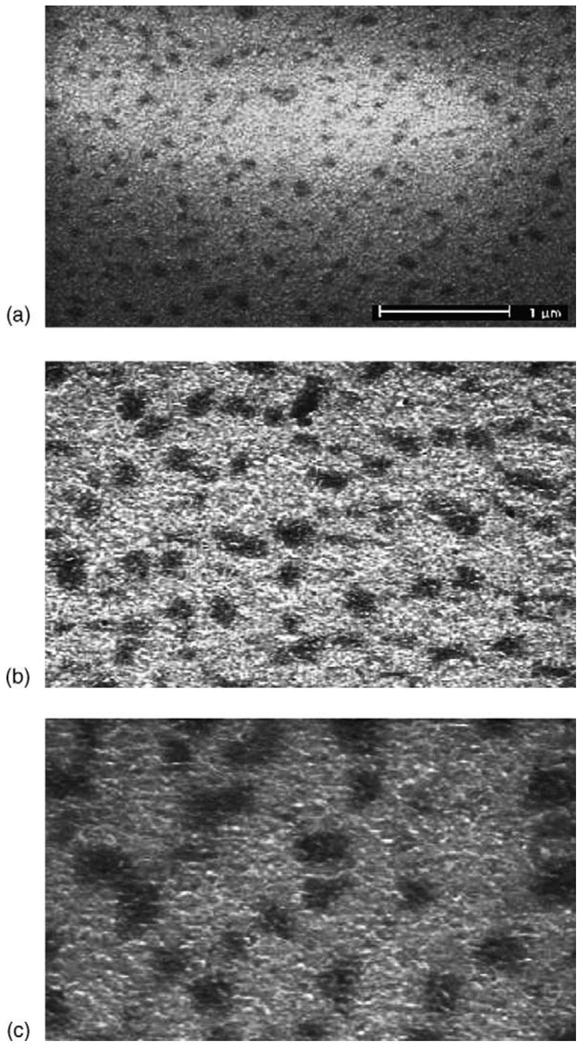

Fig. 1. Micrographs of GaAs samples annealed at 650 °C (a), 700 °C (b) and 750 °C (c) for 30 min.

were detected on the surface of each sample. One of the regions had the appearance of small ''islands'' immersed in a predominant region. A progressive increase of the size of these islands was observed as the annealing temperature increased. Furthermore, the density of islands decreased as annealing temperature increased. The microanalysis of these samples revealed a decrease of the Ga and As atomic concentrations with the annealing temperature.

Using the digital camera of the micro-Raman system, it was observed two types of regions in the surface of each annealed GaAs sample tested by EDX. One of these regions, which was characterized by a series of very small points, was immersed in the other (predominant) region. Although it was not possible to correlate directly with the two regions observed in the micrographs, it was perfectly possible to perform micro-Raman measurements of both regions displayed in the camera.

Fig. 2 shows micro-Raman spectra of the predominant region in the surface of the same annealed GaAs samples as well as the spectra of bulk GaAs. The features at about 199 and 259 cm^{-1} are characteristic of E_g and A_{1g} optical phonons of crystalline As, while the peak at about 291 cm^{-1} is the longitudinal optical (LO) phonon from GaAs. A slight downshift of the frequencies of all optical phonons of annealed GaAs samples was observed as annealing temperature increased. Moreover, the activation of the transverse optical (TO) mode at about 270 cm^{-1} was observed in the spectra of each annealed sample. The presence of this feature in the Raman spectra is an evidence of the defect formation and/or misorientation of the GaAs-[1 0 0] matrix. The increase in the relative Raman intensity of the modes of As ($I_{A_{1g},E_g}/I_{LO}$) with the annealing temperature can be attributed to an increase in the amount of crystalline As in the predominant region.

The micro-Raman spectra of the very small regions presented intense and well-defined Raman lines of TO phonon, especially for the samples treated at 650 and 700 °C, while the Raman intensity of the other lines (E_g, A_{1g} and LO) decreased drastically (Fig. 3). This observation can be interpreted as indicative of very small recrystallized regions. The analysis of the ratio between the Raman intensity of TO to LO phonons suggested, according to the Raman selection rules, that the GaAs recrystallization had occurred in the [1 1 1] direction. Moreover, investigation of the properties of III–V compound semiconductors at high temperature had already showed evidences of [1 1 1] pits in annealed GaAs samples [8]. In the case of the GaAs sample treated at 750 °C, no substantial change was observed in the micro-Raman spectra of either the small or the predominant regions. Both regions presented the same

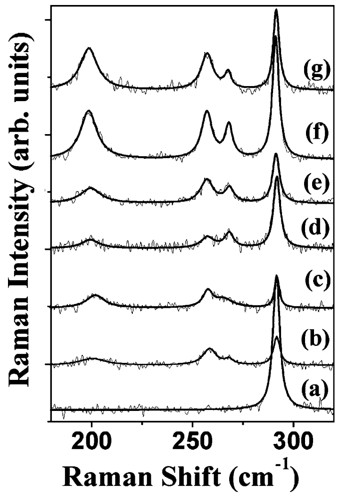

Fig. 2. Micro-Raman spectrum of bulk GaAs-[1 0 0] (a) and spectra of predominant region in the surface of GaAs samples annealed at 500 °C (b), 550 °C (c), 600 °C (d), 650 °C (e), 700 °C (f) and 750 °C (g) for 30 min.

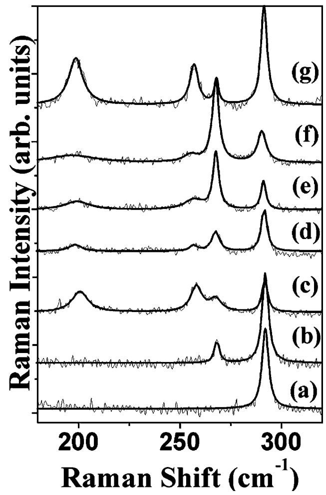

Fig. 3. Micro-Raman spectrum of bulk GaAs-[1 0 0] (a) and spectra of small regions in the surface of GaAs samples annealed at 500 °C (b), 550 °C (c), 600 °C (d), 650 °C (e), 700 °C (f) and 750 °C (g) for 30 min.

characteristic As-rich spectra, which was attributed to substantial quantity of crystalline As formed in the surface of annealed GaAs sample. The above results indicate that the As segregated tend to agglomerate and to form As precipitates in the surface.

3.2. GaSb

Fig. 4 displays micrographs of annealed GaSb samples. As can be observed, the sample treated at 350 °C showed two distinct regions in the micrographs, while the micrographs of the two samples treated at 400 and 450 °C revealed only one region with small surface cracks (splits). The microanalysis of the all annealed samples revealed double the number of Sb than of Ga atoms, as well as the fact that the Sb concentrations increased as annealing temperature increased. This means that there is excess of Sb in the superficial regions of the annealed samples. Similarly to the results of the annealed GaAs samples, no significant differences in either Ga or Sb atomic concentrations were observed in the two different regions of the 350 °C annealed GaSb sample surface. For this reason, it was impossible to chemically identify the regions by EDX microanalysis.

In contrast to the micrographs, the digital camera of our micro-Raman system showed images of two types of regions in the surface of the same annealed GaSb samples tested by EDX. Very small regions immersed in predominant regions, such as those observed in annealed GaAs samples, were also observed in GaSb samples and their sizes were sufficiently large to obtain micro-Raman spectra from them.

Fig. 5 shows micro-Raman spectra of predominant regions in the surface of the annealed GaSb samples. The features appearing at about 112 and 155 cm^{-1} are the E_g and the A_{1g} optical phonons characteristics of crystalline Sb. The Raman line at about 236 cm^{-1} is the LO mode of GaSb matrix. The activation of the TO

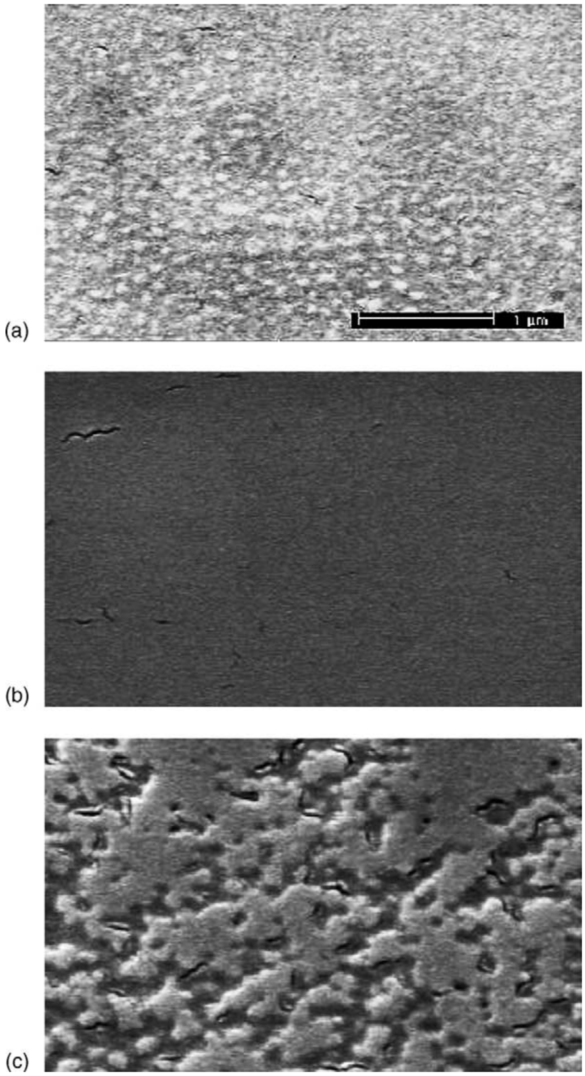

Fig. 4. Micrographs of GaSb samples annealed at 350 °C (a), 400 °C (b) and 450 °C (c) for 15 min.

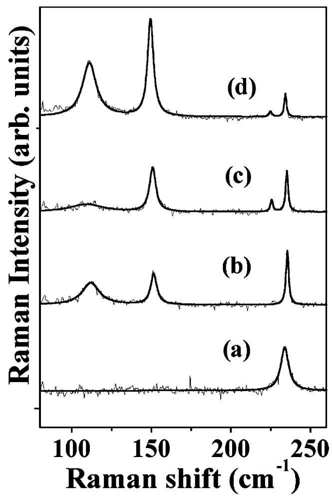

Fig. 5. Micro-Raman spectrum of bulk GaSb-[1 0 0] (a) and spectra of predominant region in surface of GaSb samples annealed at 350 °C (b), 400 °C (c) and 450 °C (d) for 15 min.

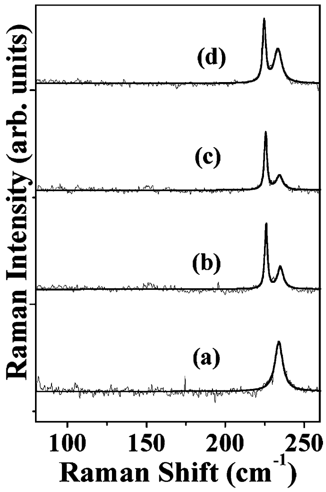

Fig. 6. Micro-Raman spectrum of bulk GaSb-[1 0 0] (a) and spectra of small regions in the surface of GaSb samples annealed at 350 °C (b), 400 °C (c) and 450 °C (d) for 15 min.

mode (at about 226 cm^{-1}) shown in the Raman spectra of annealed GaSb-[1 0 0] samples evidences structural disorder. Furthermore, the decreasing (increasing) of Raman frequency (linewidth) of LO phonon as annealing temperature increased was a strong evidence of the increasing structural disorder. On the other hand, the E_g and A_{1g} modes observed in the spectra of GaSb samples treated for 300, 400 and 450 °C can be attributed to the excess of Sb in the surface of these samples. The EDX microanalysis corroborates this interpretation. Although these temperatures are normally used to make ohmic contacts in GaSb, it was clear that they are high enough to cause an important chemical and structural disorder.

Fig. 6 shows micro-Raman spectra of very small regions immersed in the predominant region of the annealed GaSb samples. The intensity of TO modes showed a considerable increase as the annealing temperature increased, while the E_g and A_{1g} modes were not observed for any annealing temperature. Moreover, one can see that the TO mode was more intense than the LO mode for all annealed samples. On the other hand, the slight decrease of LO Raman linewidth observed on the Raman spectra of the annealed samples is strong evidence of good crystalline quality. Thus, based on these results one can conclude that the surfaces of annealed GaSb samples are composed of very small regions crystallized in the [1 1 1] direction immersed in a damaged GaSb and Sb-rich predominant region.

4. Conclusions

EDX analyses in the surface of annealed GaAs and GaSb samples showed the existence of two distinct regions, consisting of small circular regions as islands immersed in a predominant region. Although it was impossible to chemically identify the small regions by microanalysis, in the case of GaSb, excess of Sb was detected in all samples. Furthermore, the Sb concentration in the annealed GaSb samples increased with the annealing temperature, while the As concentration in the annealed GaAs samples presented a slight decrease.

The micro-Raman results corroborates the evidence of two different regions in the surface of annealed GaAs and GaSb samples, since the spectra of one region presented considerable differences from the other. The most notable difference was the activation of the TO mode followed by the decrease of linewidth of the Raman lines of LO mode in the spectra of very small regions, which was interpreted as indicating GaAs and GaSb recrystallization in the [1 1 1] direction. On the other hand, the spectra of predominant regions showed general characteristics of chemical and structural disorder in the annealed GaAs and GaSb-[0 0 1] matrices as the annealing temperature increased.

This work calls attention to the superficial chemical and structural damages in III–V semiconductor materials caused by procedures involving thermal annealing which are responsible by the degradation of transport properties and devices performance. Furthermore, our micro-Raman experiments demonstrated the sensibility of this technique to detect short-range structural defects and the chemical composition of distinct superficial regions.

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