In$_x$Ga$_{1-x}$As obtained from independent target via co-sputtering deposition

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Abstract. This paper is focused on the preparation of InGaAs thin films on GaAs substrates by r.f. magnetron sputtering technique, using the sputtering power as control means for the formation of different stoichiometries. Results of X-ray and Raman spectroscopy allowed corroborating the formation of In$_x$Ga$_{1-x}$As in different concentrations, identifying peaks associated with crystallographic planes (X-rays) and characteristic vibrational phonon modes (Raman). An analysis performed with the Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS) techniques, allowed discussing on the composition in each of the layers. Finally, an alternative in obtaining the ternary semiconductor with polycrystalline structure and preferential growth along the direction (111) was demonstrated and generated by a technique different from the epitaxial techniques, which are commonly used for the growth of III-V semiconductors.

1. Introduction
The use of non-epitaxial techniques for the preparation of ternary III-V semiconductors at laboratory scale has gained interest during the last decade due to a reduction of the costs that could be generated in the optoelectronic industry [1-5]. One of the most versatile and most commonly used techniques for the generation of materials in thin film form is magnetron sputtering, which makes it one of the most widely used technique for large scale materials production [6]. It is worthwhile mentioning that one of the most promising ternary III-V semiconductor is InGaAs, since it is possible to modify its optoelectronic properties by varying the concentration (x) of In, associated with the replacing of Indium atoms with
Gallium atoms in the GaAs matrix [7-9]. Accordingly, our efforts have been focused on the preparation of InGaAs thin films on GaAs substrates through magnetron sputtering technique, using sputtering power as a control means for different stoichiometries when depositing thin films. Evidence of said behavior is corroborated by structural, morphological and compositional characterization techniques.

2. Experimental

InGaAs thin films were deposited by magnetron sputtering r.f. on GaAs substrates (conventional cleaning) in an atmosphere of Argon at a pressure of 5 x 10⁻² Torr for 60 minutes at a temperature of 580 °C. During sputtering process, targets of Gallium Arsenide and Indium (two inches and one inch, respectively) were used. In the InGaAs growth (by co-sputtering technique), sputtering powers of 50 Watts for Gallium Arsenide and 4, 6, 8 Watts for the Indium target were used. The structural characterization of thin films was performed by means of the X-ray diffraction technique on a PANalytical Xpert Pro machine/instrument/system, equipped with a radiation source of Cu Kα (λ = 1.540562 Å) at a speed of 1 ° / min, in a range of 20 ° ≤ 2θ ≤ 40 °. Raman microscopy measurements were performed using a backscattering configuration, perpendicular to the sample, and using the 632.8 nm line of a He-Ne laser, in a Dilor XY Labram spectrometer, equipped with an Olympus BX40 microscope. The morphological characterization was made by Field Emission - Scanning Electron Microscopy (FE-SEM) at different magnifications, in a JEOL JSM740 1F instrument. Finally, a compositional study was conducted by using the XPS technique in an Alpha 10 Hemispherical Analyser machine, equipped with an X-ray tube with double anode Mg Kα eV and Al Kα lines, which provides energies of 1253.6 eV and 1486.6 eV, respectively. SIMS analyzes were performed on a SIMS-IMS GF system, which is equipped with a primary beam energy of 5 keV with an approximate angle of 45 ° with respect to the sample. CsM+ secondary ions (M is the element of interest) were analyzed using a Double-focusing mass spectrometer equipped with a photomultiplier. The samples, in all cases, were scanned in an area of 100x 100 μm. The ions emitted from the central region of the sample were focused on the mass spectrometer.

3. Results

3.1. X-Ray

Figure 1 shows x ray spectra of InGaAs thin films deposited on GaAs substrates (100). These spectra show that the peaks (in 2θ) are shifted to smaller angles compared to the characteristic values of Gallium Arsenide, which is a good indicative of the formation of the ternary semiconductor. A preferential growth along the (111) direction is observed. Indium segregation in the semiconductor is discarded, reverse to the reported when it is deposited on other substrates [10]. The crystallite size of the layers was estimated using Scherrer formula using (111) plane (results are shown in the inset of Figure 1). Finally, a first approximation to the composition of ternary InGaAs was performed using Vegard's law [11]. Values of x = 7.73%, 17.0% and 19.50% for 4 W, 6 W and 8 W target powers were found.

3.2. Raman

In the first-order Raman spectra shown in Figure 2, TO and LO Raman modes of InAs and GaAs are observed. A deconvolution made in Raman spectra using Lorentzian functions allowed determining the position of each vibrational mode. In all spectra, a shift (Δω) in frequency (cm⁻¹) of the TO-InAs mode for the sample prepared at different Indium sputtering powers (4W, 6W and 8W) was observed, regarding to the TO mode (InAs bulk) located at 221 cm⁻¹. The shift (Δω) is a combined effect of stress due to parameter lattice mismatch between InGaAs layer and GaAs substrate, and allowing because the Ga atom are substituted by In atoms into GaAs matrix during growth. The Raman spectra show that the intensities ratio (I_LO/I_TO) of the LO and TO GaAs and InAs modes is larger than one, which is an indication that the samples have a high crystalline structure.
3.3. SEM

Figure 3 (a) shows a micrograph for InGaAs layer prepared with the lowest sputtering power. This sample presents a lowest roughness compared with the sample prepared to higher sputtering power [Figure. 3 b) and c)]. In Figure 3 (b), surface changes (some voids) are observed, due to increase in the lattice mismatch between layer and substrate, associated with increasing Indium content. Finally, in G3 layer, shown in Figure 3 (c), this phenomenon is more evident, the surface is more roughness that previous ones, due to the formation and agglomeration of particles (clusters) about 150 nm diameter.

Although a change in morphology of the layers with the sputtering power (or indium content) is observed, Indium segregation and secondary phase’s formation are discarded.

3.4. Compositional

3.4.1. SIMS. From SIMS depth profiling results, the distribution of the elements was determined. In Figure 4, we show only the spectrum for the InGaAs sample grown on a GaAs substrate at a 6W indium target power. The interface between the InGaAs layer and the substrate is clearly identified. The sample
is homogeneous in composition because, the As, Ga and In signals intensity remains constant throughout the entire thickness. Traces of oxygen, nitrogen and carbon was not observed.

3.4.2. XPS. The Survey spectrum (Figure 5) corresponds to an InGaAs thin film in a region of 0-1200 eV. In this spectrum, characteristic states of InGaAs exposed to the environment, as well as Auger signals, characteristic of the ternary alloy, are observed. High-resolution measurements in the regions corresponding to Ga3d and As3d allowed the discretization on the behavior of the sample surface after being exposed to the environment. In said process, from a comparison of - In2O3 metal states, it can be demonstrated that As oxides are more volatile than Ga oxides. Spectra of the Ga were taken in the region between 14-24 eV (Figure 6). In this spectrum, from best fitting (blue line) on the experimental data the Ga hybridization states was identified.

In all spectra, a similar behavior is observed. However, only significant difference in the FWHM of In4d state (narrow spectrum from 14 to 24 eV) is found.

The binding energies calculated for Ga3d are in good agreement with that reported for the ternary semiconductor [13]. The present GaO is attributed to surface contamination post-process of sample preparation. The trace of GaO detected by XPS is due to the fact that it is a superficial analysis technique with a maximum penetration depth about 9 nm. In the same spectrum, a signal associated to In3d state is shown, which depends on Indium concentration.

In the As spectra taken in 38-48 eV region (Figure 7), a similar analysis was performed. In this spectrum, the binding energy of As3d is also in good agreement with reported value for the ternary. Although hybridization states with oxygen As+3 are identified, the lowest levels of As oxidation are due to the high growth temperature, promoting either the formation or the not desorption of unstable oxides.

As for the states associated to Indium, in additional to the aforementioned 4d state, 3d state was observed in the narrow spectra taken in the 438-456 eV region. In each spectra, the In3d3/2 and In3d5/2 doublet was identified. In the layers deposited at Indium sputtering powers of 6 and 8 Watts (spectra not shown here), there are a change in its intensity, and FWHM of each of the signals, which is attributed to Indium concentration changes.
4. Conclusions

It was found that the sputtering power allow varied the Indium content and/or the stoichiometry of the semiconductor at power lower than 8 Watts. Ternary InGaAs alloy present a preferential orientation along the direction (111), due to combined effects the stress and alloying. Finally, a dependence on its morphological properties as a function of the sputtering power was found.

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