The evolution of arsenic excess induced by thermal annealing in arsenic-rich Ga$_{1-x}$As$_x$ films

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ABSTRACT The evolution of As excess in As-rich Ga$_{1-x}$As$_x$ films is analyzed for distinct As concentrations and different annealing temperatures. Initially the samples are amorphous and crystallize partially after thermal annealing. The formation of both amorphous and crystalline As clusters is examined by micro-Raman and X-ray diffraction analysis. When highly and moderately unbalanced materials are compared, differences are clearly observed concerning the crystallization temperature and the migration kinetics of the As excess. These differences are explained by the formation of As precipitates around the GaAs crystallites in the moderately unbalanced material, contrasting with the migration of the As excess to the film surface in the highly unbalanced material.

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1 Introduction

The behavior of disordered As-rich Ga$_{1-x}$As$_x$ is especially important to understand the interface characteristics of a number of multilayered structures [1–5]. GaAs epilayers grown at substrate temperatures below 300 °C (LT-GaAs) are As rich and, after annealing at 600 °C, display a high resistivity and a short carrier lifetime, properties that make this material interesting for device applications [1]. As-grown LT-GaAs layers containing 1.0–1.5 at% excess arsenic present AsGa antisite defects [2]. Annealing at temperatures above 400 °C results in the clustering and precipitation of arsenic in the GaAs layer [3]. Arsenic precipitates formed during annealing are usually crystalline, but amorphous precipitates have also been observed [4]. One key point in considering this problem is the role of the As excess in the material and its evolution under thermal annealing. Baker et al. [5] found, from extended X-ray absorption fine structure (EXAFS) on the amorphous Ga$_{1-x}$As$_x$ system, that the As coordination changes from fourfold at stoichiometric to threefold at As-rich films, while the Ga coordination remains fourfold at all x ranges, allowing a minimum number of homopolar bonds. In As-rich a-Ga$_{1-x}$As$_x$, it was observed that the As excess is uniformly scattered in the lattice [6] and that annealing at 510 °C induces the formation of crystalline arsenic clusters [7]. However, there is no report analyzing the mechanism of evolution of the As excess during the thermal annealing in amorphous and crystalline Ga$_{1-x}$As$_x$ with a highly unbalanced degree. Even though the characteristics of the As-rich GaAs under annealing are not directly comparable to the properties of the LT-GaAs layers, the properties of the former are probably similar to the interface characteristics of LT-GaAs, since the As excess tends to accumulate in the interface of multilayered structures after annealing [4]. In this way, the characteristics of As-rich Ga$_{1-x}$As$_x$ are similar to the characteristics of the LT-GaAs surface layers.

The present report approaches the influence of thermal annealing on the structural properties of As-rich amorphous and crystallized GaAs films prepared by flash evaporation. Samples with moderate (A: $C_{As} = 55$ at%) and highly (B: $C_{As} = 68$ at%) unbalanced initial compositions were studied. X-ray diffraction (XRD) and Raman scattering were the main experimental probes used to characterize the as-grown and annealed samples. We analyzed the distribution of the As excess, and the As segregation induced by crystallization.

2 Experimental

Amorphous GaAs films 1-µm thick were deposited on glass substrates at 40 °C using the flash-evaporation [7] technique. This technique is especially suitable to provide the material with high As excess without clustering. The starting material was 6N purity GaAs and As powders. In sample A (Ga$_{0.45}$As$_{0.55}$) only pure GaAs powder was used, such that the off-balanced stoichiometry was due to the deposition parameters, while the unbalanced composition of sample B (Ga$_{0.32}$As$_{0.68}$) was attained by using a powder mixture of As and GaAs. The compositions of the samples were measured by energy-dispersive X-ray spectroscopy (EDS). The thermal annealing of the samples was performed in a furnace in Ar atmosphere for 20 min at different temperatures ($T_{ann}$). The films present a high degree of surface roughness characteristic of the flash-evaporation preparation but no As-cluster formation was observed after analysis in the scanning electron microscope. After annealing, the As concentration decreased slightly in sample A and strongly in sample B: the final A...
concentrations of these samples were 53 and 30 at %, respectively. The 5145 Å line of an Ar\(^+\) laser was used as the excitation source, and a Jobin-Yvon T-64 000 triple monochromator was used to analyze the scattered light. X-ray diffractograms were measured in the \(\theta\)–2\(\theta\) configuration to check the crystallization of the films.

3 Results

Figure 1 shows the Raman-scattering spectra of two As-rich a-GaAs samples (A and B) in the as-grown condition and after annealing. The spectra of the as-grown samples present broad bands centered at about 250 cm\(^{-1}\) and 235 cm\(^{-1}\) in samples A and B, respectively. These bands are similar to the ones obtained by other authors [8, 9]. This mode broadening is due to the breakdown in the \(k\) selection rules. After annealing at 550 °C, the Raman spectrum of sample A showed two intense peaks at 264 cm\(^{-1}\) and 287 cm\(^{-1}\), associated with the TO and the LO vibration modes of c-GaAs, respectively [10]. Two extra peaks, located around 200 and 253 cm\(^{-1}\), are associated with the optical vibration modes of the As clusters. These peaks are ascribed to the \(E_g\) and \(A_{lg}\) Raman-active phonons [11] of c-As. The Raman spectrum of sample B (at \(T_{\text{ann}} = 550\) °C) shows an intense broad band ascribed to the As phonon modes mentioned above, with a shoulder at 285 cm\(^{-1}\), corresponding to the LO mode of c-GaAs. In addition, a convoluted peak structure with centers around 255 and 265 cm\(^{-1}\) is associated with the \(A_{lg}\) mode of c-As and the TO mode of c-GaAs, respectively. In this annealing condition (550 °C) the \(E_g\) mode is almost completely lost, probably due to a larger broadening of the corresponding band. At \(T_{\text{ann}} = 600\) °C, sample B presents intense peaks, characteristic of \(E_g\) and \(A_{lg}\) vibration modes of c-As, and two weak shoulders at 265 cm\(^{-1}\) and 285 cm\(^{-1}\), corresponding to the TO and LO modes of GaAs.

Figure 2 shows the diffractograms of samples A and B. The amorphous structure of the as-grown films is clear. In con-