Revista Colombiana de Materiales N. 5 pp. 369-374

Edición Especial Artículos Cortos

MULTILAYERS GROWTH OF $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ USING A SOLID-ARSENIC-BASED MOCVD SYSTEM

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ABSTRACT

We reported the results of the studies related to the growth and characterization of $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ epitaxial heterostructures obtained by MOCVD using solid arsenic as arsenic precursor instead arsine as is used in conventional MOCVD systems. The use of metallic arsenic introduce important differences in the growth process due to the absence of the hydride group V precursor (AsH_3) that is manifested in the electrical and optical characteristics of GaAs and its alloys. The most serious difficulty for growing $Al_xGa_{1-x}As$ and GaAs epitaxial layers by arsenic-based-MOCVD is the incorporation of large amount of residual impurities as carbon and oxygen that comes from the organometallic compounds. Additionally, the surface morphology of the final layers present a high roughness degree that makes impossible the fabrication of quantum effects based devices with optimal optical properties, although these layers can be used for fabricating other types of multilayer based devices. The homogeneity of the samples was evaluated by low-temperature photoluminescence and Raman spectroscopy.

Keywords: *Elemental arsenic, MOCVD,* $Al_xGa_{1-x}As/GaAs$*, Surface morphology*

RESUMEN

Reportamos los resultados de los estudios relacionados con el crecimiento y caracterización de $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ heteroestructuras epitaxiales obtenidos por MOCVD con arsénico sólido como precursor del arsénico en lugar de arsina como se utiliza en sistemas MOCVD convencionales. El uso de arsénico metálico introduce diferencias importantes en el proceso de crecimiento, debido a la ausencia del grupo precursor de hidruro (AsH_3) que se manifiesta en las características eléctricas y ópticas del GaAs y sus aleaciones. La dificultad más grave para el crecimiento de capas epitaxiales de $Al_xGa_{1-x}As$ y GaAs por MOCVD-basado en arsénico es la incorporación de una gran cantidad de impurezas residuales como el carbono y el oxígeno provenientes de los compuestos organometálicos. Además, la morfología superficial de las capas finales presentan un alto grado de rugosidad que hace imposible la fabricación de dispositivos basados en efectos cuánticos con propiedades ópticas óptimas, aunque estas capas se pueden usar para la fabricación de otros tipos de dispositivos basados en múltiples capas. La homogeneidad de las muestras fue evaluada por fotoluminiscencia a baja temperatura y espectroscopia Raman.

Palabras clave: *Arsénico elemental, MOCVD,* $Al_xGa_{1-x}As/GaAs$*, Morfología superficial*

1 INTRODUCTION

The fabrication of modern electronic devices based on $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ epitaxial layers as; high electron mobility transistors, lasers, optical modulators, among others, require the growth of epitaxial layers with the purity and crystalline perfection demanded for optoelectronic applications [1]. The metal organic chemical vapour deposition (MOCVD) system has been widely used for the growth of epitaxial semiconductors layers with high quality and excellent surface morphology, however, this technique has as main problem the use of highly toxic gases, as is the case with the use of arsine. Liquid Phase Epitaxy (LPE) has as main problem the thickness control and surface morphology, the Molecular Beam Epitaxy (MBE) is an expensive growth system in reference to the initial investment and the operation costs. As we mentioned before, MOCVD has as main problem the use of toxic gases. The use of nonconventional MOCVD systems, in which the arsine has been substituted by solid arsenic, is cheaper and safer [2]. In this paper, we are presented the obtained results using solid arsenic for the growth of epitaxial multilayers. The initial goal was the evaluation of this system for growing complex devices as multiquantum wells, as is routinely made with the traditional MOCVD systems.

2 EXPERIMENTAL DETAILS

The $Al_xGa_{1-x}As$ was grown on semi-insulating (100) Cr-doped GaAs substrates, ±4° misoriented with respect to the (110) direction. The substrate preparation involves, as usually, degreasing by organic solvents, surface oxide elimination by HCl and a surface chemical etching using $H_2SO_4:H_2O_2:H_2O$ (5:1:1). The layers were grown using electronic grade trimethylgallium (TMG) and trimethylaluminium (TMA) as gallium and aluminium precursors, respectively, and metallic arsenic (9N) as the arsenic source. The main characteristics of the MOCVD reactor were reported elsewhere [3]. The MOCVD system consists of a horizontal quartz tube operating at atmospheric pressure. The substrates were placed on a graphite substrate holder and heated by infrared lamps. The arsenic supply was controlled by a second independent furnace. The III/V ratio used in the growths was adjusted by controlling the arsenic source temperature and controlling the hydrogen flow through the metallorganic vessels by means of electronic mass flow controllers. The growth atmosphere consisted of palladium purified hydrogen. For growing the main GaAs layer after the first barrier, one has to wait a time in order to purge the growth chamber for obtaining abrupt interfaces; the chosen interruption times were between 0 to 15 min, For growing the last barrier, in some cases a small interruption time was performing (>2min) but in the most cases there was not any interruption, see Fig. 2.

Figure 1. No scale schematic diagram of grown structure with a GaAs quantum well.

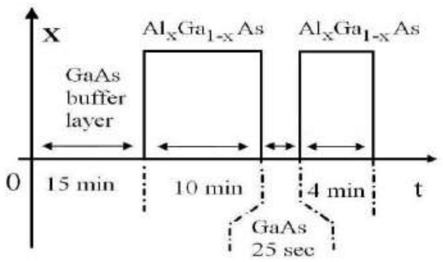

Figure 2. Time diagram of sample C11.

3 EXPERIMENTAL RESULTS AND DISCUSSION

SIMS composition profile for a typical sample demonstrates the successful growth of a structure with a single quantum well, see Fig. 3. In this sample, the GaAs quantum well was grown at 25 s for a thickness expected of ~10 nm. From the measurements of Raman scattering, the concentration estimated of aluminium in the $Al_xGa_{1-x}As$ layers is x~0.25 [4]. The interruption time before the growth of the GaAs cladding layer was 2 min. The SIMS profile shows an average thickness of around 46 nm, which is much larger than expected, additionally, the aluminium concentration curve in the quantum well does not return to the background SIMS level. These effects can be attributed to the penetration depth of the ions used for sample erosion during the measurement and the effect of the surface roughness over depth resolution [5] among other factors. The main residual impurity profiles were explored; these are showed in Fig. 4, which are silicon, carbon and oxygen [6]. In the SIMS profile can be observed, the silicon concentration in the $Al_xGa_{1-x}As$ films always stayed above the detection level. The sample presented in this profile was the C11, which was grown in a substrate doped with silicon with a concentration of ~$1x10^{18}$ cm^{-3}. In the region of the buffer layer the silicon concentration is reduced at the SIMS detection limit for silicon. In the $Al_xGa_{1-x}As$ layers, the silicon concentration slightly reaches a higher concentration of $1x10^{19}$ cm^{-3}. According to the observations from the studied samples, the source of contamination by silicon is the aluminium precursor (TMAl) [7]. From the measurements by Hall effect performed in similar samples, the silicon behaves like donor impurity, So it can be concluded that silicon is the impurity that determines the type of conductivity in the films. Although silicon is from group IV can also act like an acceptor impurity; in the $Al_xGa_{1x}As$ grown in vapour phase, it has been demonstrated that introduces a single donor level [8]. As has been observed, the carrier concentration measured by Hall effect corresponds approximately to the silicon concentration measured by SIMS and the growth temperature does not affect to a large extent the final silicon concentration [7]. In the reports on AlGaAs grown by MOCVD has been found that high growth temperatures (~850°C) cause greater carbon incorporation [8]. According to the SIMS measurements, one would expect a layer thickness of ~100 nm, but the thickness of this grown layer is not enough thin for the observation of quantum effects.

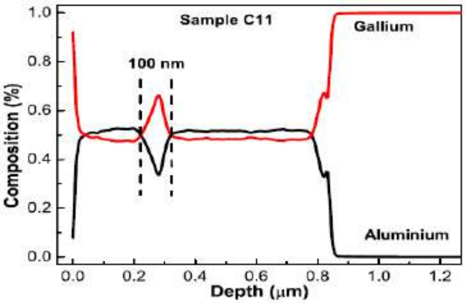

Figure 3. Concentration profiles of aluminium and gallium measured by SIMS.

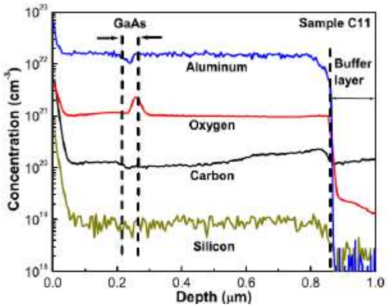

Figure 4. Concentration profiles of residual impurities and Al in the sample C11.

As can be observed in Fig. 3, as in the case of sample C11, the thickness of the GaAs layer was about 100 nm, but this is not clear from the SIMS curves presented in Fig. 4. The peak of the oxygen concentration curve is in the first interface GaAs on $Al_xGa_{1-x}As$, this suggests an accumulation in this interface. In order to assess the optical radiation of these samples, 10 K photoluminescence was performed, for this measurement it was used an He-Ne laser with a 20 mW as nominal power, and 632.8 nm as main line, the sample was mounted in a close cycle He cryostat, special care was take in order to avoid the unintentional strain of samples. Fig. 5 shows the PL spectrum for sample C11. The peaks at 1.494 and 1.514 eV correspond to the GaAs substrate emissions, from the excitonic band and from the acceptor band identified the emission of carbon as acceptor impurity. The peak at 1.8 eV has been identified as an emission of the $Al_xGa_{1-x}As$, although in this peak are contained the emissions due to the excitonic and the acceptor transitions. Additionally, this peak has a weak intensity compared with the intensity of substrate peaks that can be associated with the incorporation of impurities, as has been reported [9]. The peak at 1.659 eV is not well identified but might be associated to structural defects. The association of this peak with emission in the intermediate layer is not discarded, due to the observation of this behaviour type in the PL spectra of other samples with the intermediate GaAs layer, as it will comment in the section related with the roughness, all these samples grown with solid arsenic presented a high degree of this one.

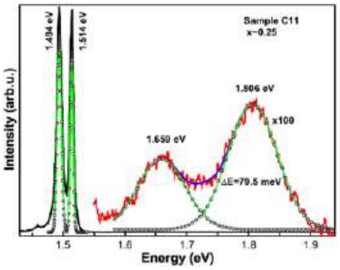

Figure 5. Low-temperature PL spectrum of the sample C11.

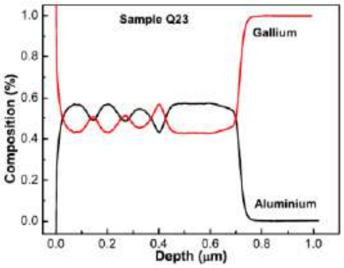

Figure 6. Multilayers structure grown with 8 layers using the arsenic-based-MOCVD.

To explore the non-conventional MOCVD system capabilities for growing multilayers structures with thicknesses near 100 nm was grown a samples set with more layers. This is the case of sample Q23, whose composition profile is showed in Fig. 6. All the $Al_xGa_{1-x}As$ layers were grown with the same experimental conditions and the same Al molar fraction and with the substrate temperature of 855°C and the arsenic source temperature of 570°C. For purging the growth chamber after the $Al_XGa_{1-X}As$ layer growth, the flows were interrupted by 10 min; this was done to assure that the interfaces were abrupt. During this time the substrate temperature was diminished at 750°C. As a result of these performed growth procedures was possible to grow the multilayer structure showed in the compositional profile, as can be observed the depth profile shows the GaAs layers and in general the multilayer structure planned, the thicknesses of these layers is too large, around 50 nm, although, it cannot be identified clearly where the GaAs layer begins and ends in this SIMS measurement. Another important feature of the samples grown with this system is the roughness presented for their surfaces. To assess the roughness degree Atomic Force Microscopy (AFM) measurements were performed. Fig. 7 shows the surface morphology of sample C11 as can be observed, there are some peaks that have heights greater than 60 nm. This roughness strongly deteriorates the optical properties of the quantum well. The obtained root mean square (RMS) of the roughness was about 18 nm. The importance of minimizing the surface roughness is for the improvement of optical and electrical properties of the sample. Although, the growth parameters were varied, the degree of surface roughness did not decrease, whereby it is thought that this roughness degree is related with the growth kinetic on the substrate surface by the use elemental arsenic. A usual explanation for the large amount of surface roughness is the very low surface mobility of aluminium during the growth process. Furthermore, as in the non-conventional MOCVD system replaces AsH_3 by metallic arsenic, it can be argued that causes changes on the surface kinetics processes for arsenic integration because of the dominant species is As_4. In traditional systems that use arsine (AsH_3), its decomposition on the growth surface provides atomic hydrogen that combines with the methyl radical to form methane, which is removed easily as a byproduct of the process. In the case of solid arsenic, these atomic hydrogens are absent, so the main by-products are ethane molecules due to recombination between the methyl radicals, in addition arsenic obtained by the sublimation of the elemental arsenic is As_4, being these species less mobile on the growth surface. Moreover, the use of solid arsenic instead arsine favours the impurity incorporation such as carbon and oxygen, in comparison with the conventional MOCVD [10]. The carbon arises from the decomposition of the TMGa and TMA molecules, which is a component, and it is not efficiently removed due to the lack of monoatomic hydrogen in comparison with the arsine decomposition processes in the conventional MOCVD system. This roughness degree is a very serious limitation if the purpose is to grow multilayer structures based in quantum effects, due to the exciton confinement and radiation; this is because the size of the confinement layer is out of precise control with this growth system, producing a weakness and wide photoluminescence signal [10]. Many authors have related the residual impurity incorporation with the increase of roughness and the poor quality of the interfaces [10]. The high resistivity and the lack of PL signal have been related to the oxygen incorporation from the residual impurities of the metal organic precursors. It is widely accepted that oxygen introduces deep traps in the GaAs and its alloys [10]. The three dominating non-radiative deep centers locate at about 0.3, 0.5 and 0.8 eV below the conduction band, which reduce critically the luminescent efficiency. Additionally, when the growth temperature is increased the deep traps concentration is reduced [11]. Fig. 8 shows Raman scattering results of epilayer C11, which presents the main signals at 275 and 377 cm^{-1} that are assigned as LO-GaAs- and LO-AlAs-like modes, respectively. The weak shoulders on the low-frequency side of the GaAs-LO and AlAs bands at 262 and 369 cm^{-1} are the GaAs-TO and AlAs-TO modes.

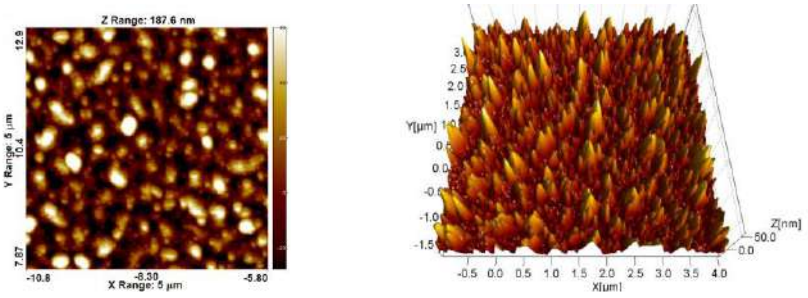

Figure 7. Typical sample roughness presented by the final surfaces, sample C11.

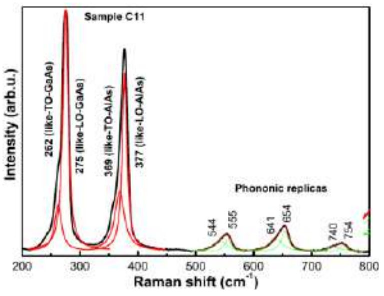

Figure 8. Raman spectrum of the sample C11.

4 CONCLUSIONS

In this work has been presented the results of $Al_xGa_{1-x}As$/ GaAs/ $Al_xGa_{1-x}As$ multilayers growth, using a non-traditional MOCVD system. This growth system uses solid arsenic instead of arsine, this feature makes it more secure compared to one that uses arsine. As is known, the use of solid arsenic instead arsine is related with large amount of incorporated impurities and a surface morphology bad. Although, the presented results show that is possible the growth of epitaxial layers with thicknesses near 100 nm as was showed by SIMS profiles. The characterization performed with AFM shows that the amount of roughness is near 60 nm. So it can be concluded that the mean limitation of the epitaxial layer thicknesses is the large amount of roughness presented by the surfaces, this is a serious problem when this layers are destined to quantum effect based devices.

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