Received: August 27, 2020. Revised: March 29, 2021. Accepted: April 26, 2021. Published: May 10, 2021.

Characterization Of N-Type $Al_xGa_{1-x}As/GaAs$ Heterostructures Grown ByElemental-Arsenic-Based-MOCVD

J. Martínez-Juárez[1], R. Castillo-Ojeda[2], , J. E. Flores-Mena[3], J. Díaz-Reyes[4], O. Zaca-Moran[4], M. Galván-Arellano[5], E. López-Cruz[6]

[1] Centro de Investigación en Dispositivos Semiconductores, ICUAP, Benemérita Universidad Autónoma de Puebla. Puebla, México

[2] Universidad Politécnica de Pachuca. Municipio de Zempoala, Hidalgo, México
[3]Facultad de Ciencias de la Electrónica, Benemérita Universidad Autónoma de Puebla, Puebla, México
[4] Centro de Investigación en Biotecnología Aplicada, Instituto Politécnico Nacional. Tepetitla, México
[5] Depto. de Ingeniería Eléctrica, SEES. CINVESTAV-IPN, México, D.F. México
[6]Instituto de Física "Luis Rivera Terrazas", Benemérita Universidad Autónoma de Puebla, Puebla, México

Abstract—**In this work we present the results of the growth and characterization of $Al_xGa_{1-x}As/GaAs$ multilayer structures obtained in anelemental-arsenic-based-MOCVD system. The main goal is to explore the ability of the system for growing high quality multilayer structures like quantum wells. The use of metallic arsenic could introduce important differences in the growth process due to the absence of the hydride group V precursor (AsH_3), which is manifested in the electrical and optical characteristics of both GaAs and $Al_xGa_{1-x}As$ layers. The characterization of these epilayers was performed using low temperature photoluminescence, Hall Effect measurements, X-Ray diffraction, Raman spectroscopy, secondary ion mass spectroscopy and Atomic Force Microscopy.**

Keywords—Elemental arsenic; MOCVD AlGaAs/GaAs epilayers; Hall effect; photoluminescence (PL); Atomic Force microscopy (AF); surface morphology; secondary ion mass spectroscopy (SIMS)

I. INTRODUCTION

Among the III-V semiconductor materials, GaAs and $Al_xGa_{1-x}As$ have been widely studied. This due to their optical and electrical properties, nowadays is very common to find a large variety of devices based on these materials: lasers for commercial CDs, high mobility transistors, electro-optical switches, and some other electro-optical devices [1]. They are only a few examples of wide field of applications of these devices made up with $Al_xGa_{1-x}As/GaAs$ heterostructures. In order to obtain these epitaxial layers with useful characteristics for the optoelectronic applications it is necessary to grow them with the adequate degree of purity and crystalline quality. Features as thickness control, the electrical and optical properties and crystal quality of the thin films are tightly associated with the growth technique used for its preparation. Molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), and metal organic chemical vapour deposition (MOCVD) are the most successful ones for depositing the $Al_xGa_{1-x}As/GaAs$ heterostructures. 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 and phosphine, both chemical compounds are used as precursors of the III-V semiconductor compounds. Liquid phase epitaxy (LPE) has as main problem the thickness control and surface morphology, the molecular beam epitaxy uses 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 [2,3].

In this work we present the results obtained using one of these growth systems, in which the use of arsine has been substituted by elemental arsenic. Solid arsenic is safer due to its low vapour pressure at room temperature and it is easy to store.

II. 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). As a last step, the substrates were rinsed in deionized water, and the GaAs wafers were dried by nitrogen blowing to eliminate any water trace. 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 [4]. 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 can be easily adjusted by controlling the arsenic source temperature or/and controlling the hydrogen flow through the metallorganic vessels by means of electronic mass flow controllers (MFC). The growth atmosphere consists of palladium purified hydrogen (H_2).

For the low-temperature photoluminescence (LT-PL) measurements the samples were mounted on a cold finger of a liquid helium cryostat. It was used as over gap excitation the 632.8 nm line of a helium-neon laser, with a nominal power density of 15 mW/cm^2. Emitted radiation was detected with an GaAs:Cs photomultiplier R636 Hamamatsu and analyzed through an Anton monochromator. For studying the $Al_xGa_{1-x}As$ layers composition and their homogeneity Raman spectroscopymeasurements were performed on the grown samples. Raman scattering experiments were carried out at room temperature using the 5145 Å line of an Ar^+-ion laser at normal incidence for excitation. The light was focused into a spot of 6.0 µm diameter on the sample using a 50x (numerical aperture 0.9) microscope objective. The laser power used in these measurements was 20 mW. Care was exercised not to heat the sample inadvertently to the point of changing its Raman spectrum. Scattered light was analysed 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 time was limited to 60 sec to minimize the sample heating effects mentioned above. Absolute spectral feature position calibration to better than 0.5 cm^{-1} was performed using the observed position of Si which is shifted by 521.2 cm^{-1} from the excitation line. The electrical properties of the layers were studied using Hall Effect by the Van der Pauw method at 77 and 300 K. The investigated samples were square shaped with dimensions of 5.0x5.0 mm^2 and thickness of 0.48-2.97 µm. The samples were provided with four ohmic contacts by alloying indium small balls on the sample corners, at 400°C for 1 min in a nitrogen atmosphere. The linearity and symmetry of the ohmic contacts were tested following the procedure described in the ASTM standards [5].

III. Experimental Results And Discussion

After the substrate preparation, the first grown layer was a GaAs buffer layer with a thickness of approximately 0.2µm and in some cases 0.5µm. The substrate temperatures used for the growth of the GaAs buffer layer ranged from 600 to 875°C with an arsenic fluxof 7.0 µmol/min. This arsenic flux corresponds at 560°C for the arsenic source, in the growth system. The buffer layer surface morphology was evaluated using Atomic Force Microscopy. All the examined GaAs buffer layers presented a like-mirror aspect. Fig. 1 shows the typical surface morphology of the buffer layer, as it can be seen, the roughness of the layer is not larger than 10 nm. The growth temperature of the shown sample was ~750°C.

The surface characteristics of the $Al_xGa_{1-x}As$ epitaxial layers were very sensitive to the growth temperature. At low growth temperatures, mirror-like surfaces were obtained; as the growth temperatures (T_G) increases reaching about 750°C microscopic features appeared on the surfaces. Those features are oval defects and some other kind of typical MOCVD defects as those due to the beginning of the homogeneous phase growth regime, see Fig. 2. For growth temperature higher than 800°C the surface appeared hazy and in some cases eventually becomes polycrystalline as was examined by X ray measurements [6]. The $Al_xGa_{1-x}As$ layers were grown in a wide interval of aluminium molar concentration. In most of the cases the epitaxial layers obtained with growth temperatures below 800°Cpresented a hazy surface.

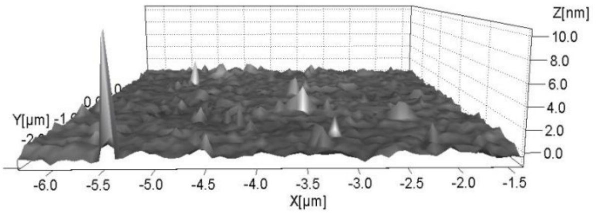

Fig. 1.Surface Morphology of the GaAs buffer layer obtained by Atomic Force Microscopy, which was grown at 750°C.

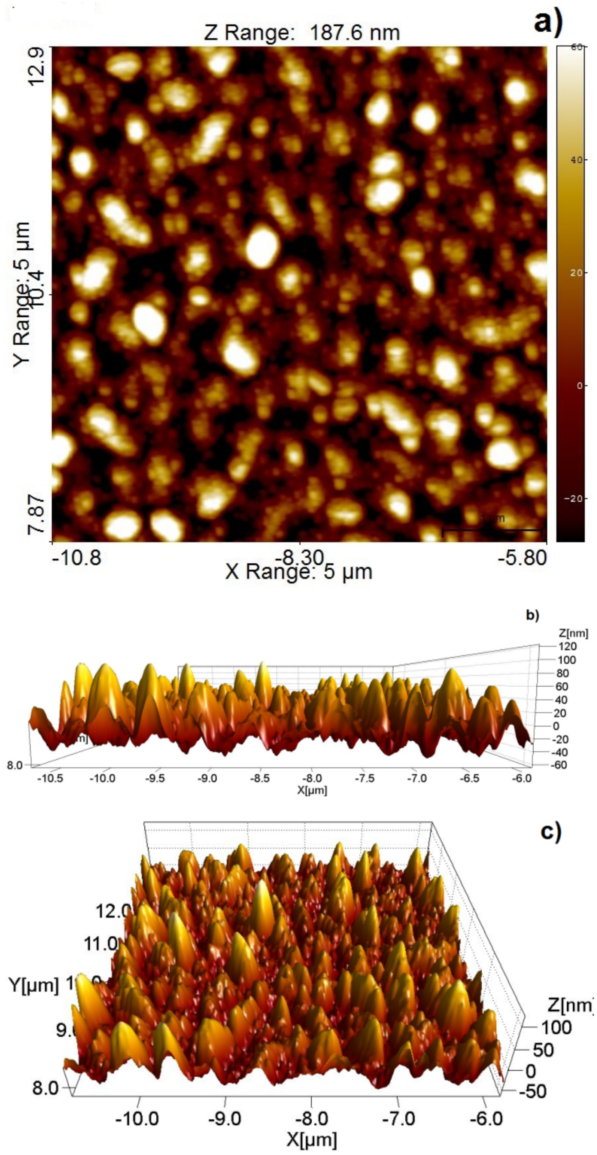

Fig. 2. An $Al_xGa_{1-x}As$ typical surface scanning by AFM, x=0.3.

In order to obtain a better assessment of the layers roughness, atomic force microscopy was carried out. At nakedeye, the sample illustrated in Fig. 2 presents nearly a mirror-like aspect but as can be seen in figure the surface presents a high roughness degree. In this AFM image, the maximum value in the vertical scale is 100 nm, see Fig. 2b. The way in which the heights are distributed on the layer surface can be appreciated in Fig. 3. This histogram has been obtained from 100 points on the surface. The more common explanation for the high roughness degree in the $Al_xGa_{1-x}As$ layers is the very low surface mobility of aluminium during the growth process. Furthermore, in the growth system in which the AsH_3 has been replaced by elemental arsenic the growth kinetic has been drastically modified. The sublimation of metallic arsenic gives as a result the dominant As_4, this species has a different surface mobility than monoatomic arsenic produced by the arsine decomposition [7, 8].

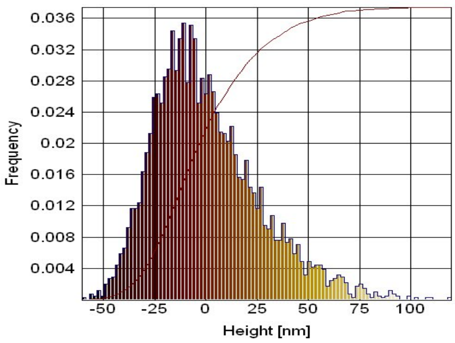

Fig. 3.Histogram of heights distribution.

As has beenpointed out,the substrate temperatures used for growing the GaAs buffer layer ranged from 600 to 875°C and the arsenic temperature was 560°C. In this range, the free carrier concentration increases as the growth temperature is increased. The electrical characterization results for $Al_xGa_{1-x}As$ layers are summarized in the Table I, at 650°C the electron concentration was approximately $7x10^{15}$ cm^{-3}, while for samples grown at ~870°C the carrier concentration was approximately $2x10^{17}$ cm^{-3}, the 300 K mobility of these layers was approximately 2000 $cm^2/V·s$. In some cases, the 77 K mobility could not be measured due to the impossibility of obtaining good ohmic contacts at this temperature. As the growth temperature was increased the carrier concentration only registered a slight increase. The Hall effect measurements at 77K shows that the grown samples are highly compensated. Several authors have reported that carbon concentration increases in a linear proportion as the growth temperature is increased. The absolute carbon concentration in $Al_xGa_{1-x}As$ epilayers could increase at levels greater than 10^{19} cm^{-3}. Although the epilayers were grown without intentional doping, nevertheless, a great amount of the incorporated residual impurities to the layers comes from the organometallics, as have been found by Spectroscopy Ion Mass Secondary (SIMS). These residual impurities are mainly carbon, oxygen and, silicon which concentrations are about 10^{18},$10^{21}$and 10^{16} – 10^{17} cm^{-3}, respectively.

From the experimental results, we may note some important facts. The electron mobility at 300 K for the $Al_xGa_{1-x}As$ epilayers grown with metallic arsenic are comparable to the mobility of the samples grown in arsine-based MOCVD systems [7,8,9]. The differences between the measured carrier concentrations with those taken from the reference [10] can be related to the presence of carbon, silicon and oxygen as residual impurities. As several authors have shown, the oxygen concentration in MOCVD AlGaAs samples lies in the range of 10^{17} to 10^{19} cm^{-3}. Otherwise, as our SIMS measurements shown, the carbon concentration can be as high as 10^{19} cm^{-3}. With reference to the role of the arsenic source in the epitaxial layer characteristics, the changes on the arsenic pressure apparently do not influence the electrical properties of the samples. As can be seen in Table I, for the samples Q39 and 126, with different growth conditions, the mobility and the carrier concentration have similar magnitudes. In fact, the room temperature mobility for all the samples varies in the range 1000 to 2500 $cm^2/V·s$, these values are in the range of those reported by other authors for arsine based MOCVD process.

TABLE I. ELECTRIC MEASUREMENTS OBTAINED BY HALL EFFECT OF $AL_XGA_{1-X}AS$ LAYERS GROWN BY MOCVD. THE TABLE CONTAINS THE SOME GROWTH PARAMETERS .

Sample	**T_G** (ºC)	**T_{As}** (ºC)	**N_{300}** (cm^{-3})	**μ_{300}** ($cm^2/V·s$)	**Resistivity** (Ω·cm)
1169	750	570	$1.34x10^{17}$	538	0.09
258	750	570	$2.33x10^{16}$	876	0.03
1235	800	570	$2.20x10^{17}$	943	0.02
126	820	585	$1.40x10^{16}$	1718	0.03
1173	850	570	$4.20x10^{17}$	1272	0.01
57	870	570	$1.70x10^{16}$	2290	0.06
Q39	875	565	$7.30x10^{16}$	1421	0.06

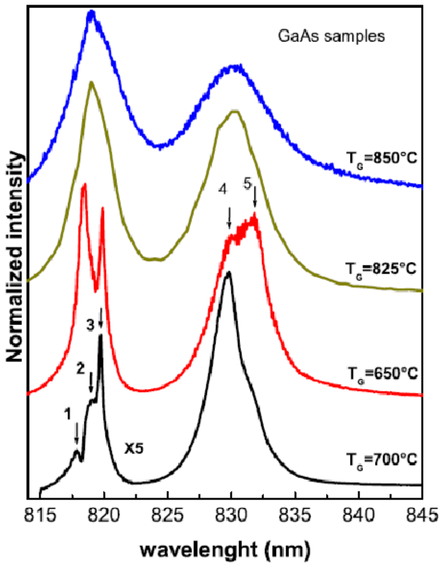

Fig. 4. GaAs buffer layers photoluminescence spectra for different growth temperatures.

Figure 4 illustrates the 12 K photoluminescence spectra of the GaAs buffer layers, which present two dominant radiative bands that are situated in the excitonic and of impurities regions. The first one is constituted by three bands that are associated at free exciton (F, X) (818.3 nm) [7, 11], labelled by 1, exciton state bound to neutral donor, $(D°,X)_{exc}$ (818.67-818.79 nm) that is titled by 2 and the labelled by 3 corresponds at J=1/2 exciton bound to neutral acceptor, $(A°,X)_{1=2}$ (819.7 nm). The peaks labelled by 4 and 5 correspond to conduction band to neutral acceptor at 830.1 nm (e-A°), and neutral donor to neutral acceptor at 832.5 nm (D°-A°). The existence of the free exciton peak in the PL spectrum demonstrates the goodcrystalline quality of the GaAs epilayers [12].

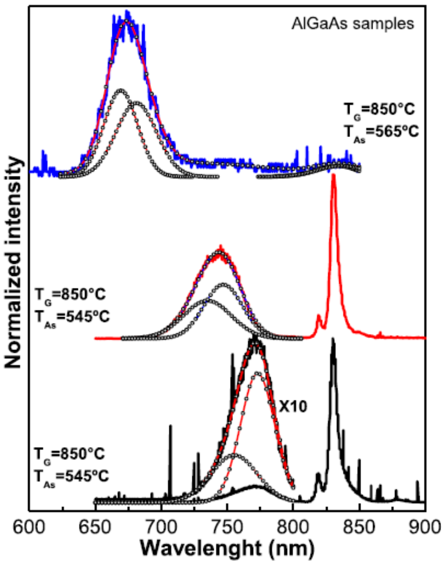

Fig. 5. Photoluminescence spectra measured at 12K of $Al_xGa_{1-x}As$ layers.

In order to obtain photoluminescence signal from the $Al_xGa_{1-x}As$ layers was necessary to grow them at temperatures higher than 800°C, which are high in comparison with the temperatures required in other growth systems as in the same arsine-based-MOCVD. The weaknesses and in some cases the lack of photoluminescence signal is associated to the great quantity of residual impurities that come from the metalorganic precursors [7]**.** It is widely accepted that oxygen is a residual impurity that introduces deep traps into $Al_xGa_{1-x}As$ [13], which are three dominating nonradiative deep centers located at about 0.3, 0.5 and 0.8 eV below the conduction band that critically reduce luminescence efficiency [12,13]. In addition, when the growth temperature is increased the traps concentration is reduced. In Fig. 5 are showed typical photoluminescence spectra of the $Al_xGa_{1-x}As$ layers studied in this work. A common characteristic of $Al_xGa_{1-x}As$ layers is the great "full width at half-maximum" (FWHM) of the peaks corresponding to the $Al_xGa_{1-x}As$ excitonic and the acceptor-donor bands. Typical values of the FWHMs of the epilayers were around 80 meV, which are associated with the incorporation of residual impurities and to the variation of aluminium molar concentration due to mass controllers. The wide and shape of this peak makes difficult to evaluate the aluminium molar concentration by low-temperature photoluminescence.

Figure 6 shows the typical Raman spectra of the $Al_xGa_{1-x}As$ samples grown by nonconventional MOCVD. The Raman spectrum presents five vibrational bands centred at 278, 377, 552, 650 and 746 cm^{-1}. The dominant bands can be associated to the GaAs, and AlAs vibrational modes. A standard fitting procedure performed in the interval of 215–450 cm^{-1} suggests this association. Such bands can be deconvoluted in four Lorentzian line shape signals as shown in Fig. 6, which are located at 268, 277, 366, and 378 cm^{-1}.

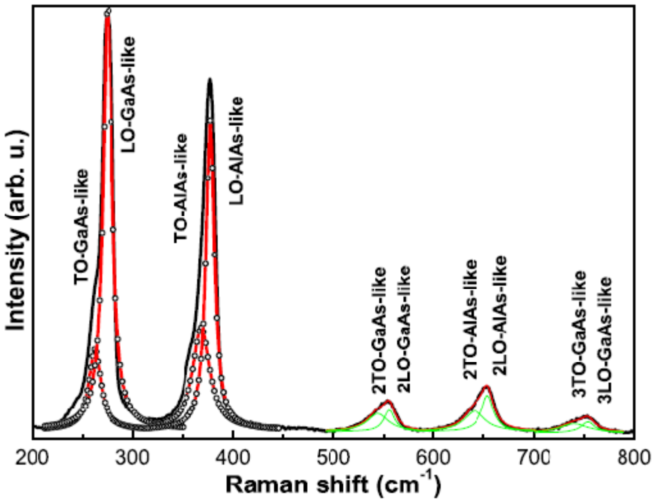

Fig. 6.Typical Raman spectrum of the $Al_xGa_{1-x}As$ samples grown by MOCVD.

Taking into account that phonons are active in the first-order Raman process in backscattering on the (001) face, one may assign our vibrational bands to the TO-GaAs-like (268 cm^{-1}), LO-GaAs-like (277 cm^{-1}), TO-AlAs-like (366 cm^{-1}) and LO-AlAs-like (378 cm^{-1}). The low frequency asymmetry of the GaAs-like mode is then obviously due to the contribution of the scattering process of phonons with nonzero **q** vectors that become active due to the alloying disorder process. The TO-GaAs mode, which in principle is forbidden in the experimental geometry for the (100) orientation of the substrate, becomes active by the breakdown of the selection rules in the backscattering configuration. This breakdown is attributed to structural defects in the alloy originated from compositional fluctuations and by elastic scattering and by the ionized doping impurities. Its appearance indicates that the crystalline quality of the $Al_xGa_{1-x}As$ layers is not perfect but in general the crystalline quality is fairly good as has been demonstrated. The modes LO-GaAs like, TO-AlAs like and LO-AlAs like, respectively, are originated on the ternary alloy. Due to the thickness of the $Al_xGa_{1-x}As$ epilayers, the modes corresponding to GaAs should not be assigned to the buffer layer. A possible explanation of the presence of the GaAs signals is the possible existence of crystalline defects in the epitaxial layers (or perhaps the origin of this signal is due to the thickness of the layer which allows the light to reach the substrate). The forbidden signals are more clearly observed for samples grown at the extreme growth conditions. Its appearance suggests that the crystal quality of the $Al_xGa_{1-x}As$ layers is not perfect, however, with the increase of the growth temperature this peak disappear indicating the improving of the layers quality. Most of the samples showed in this work were grown with high temperatures. The Al molar fraction for the $Al_xGa_{1-x}As$ samples can be determined using the fitted curves that relate the LO-phonon frequency with the aluminium content in the $Al_xGa_{1-x}As$ system [14]: From Fig. 6, one can observe that the other vibrational peaks labelled by c, d and e, which are associated with 2LO-GaAs-like, LO-(GaAs+AlAs)-like and 2LO-AlAs-like.

The chemical composition of the $Al_xGa_{1-x}As$ layers was studied by secondary ion mass spectroscopy. Fig. 7 illustrates the SIMS concentration profiles for the residual impurities detected in one of the typical $Al_xGa_{1-x}As$ layers. The main impurities are silicon, carbon and oxygen. In the case of the SIMS spectra showed in Fig. 7, whose semi-insulating substrate is doped with chrome, the silicon concentration is under the detection level. In the regions of $Al_xGa_{1-x}As$ the silicon concentration approximately acquires a constant level that can be observed in figure. In the region of the buffer layer the silicon concentration reduces until the detection limit for silicon. In the $Al_xGa_{1-x}As$ layers, the silicon concentration slightly reaches a greater concentration to $1x10^{17}cm^{-3}$. According to the profiles observed in the samples, the source of silicon contamination is the aluminium precursor (TMAl). By the measurements of Hall effect and the silicon behaviour like donor impurity, it is possible to be concluded that the silicon is the one that determines the type of conductivity in the layers. Although, the silicon is of group IV and could also act like acceptor impurity, in the growth of $Al_xGa_{1-x}As$ in vapour phase, it has demonstrated that it introduces a single donor level. As it is observed in Table I, the carriers concentration measured by Hall effect corresponds approximately to the silicon concentration measured by SIMS and the growth temperature does not affect significantly the final silicon concentration.

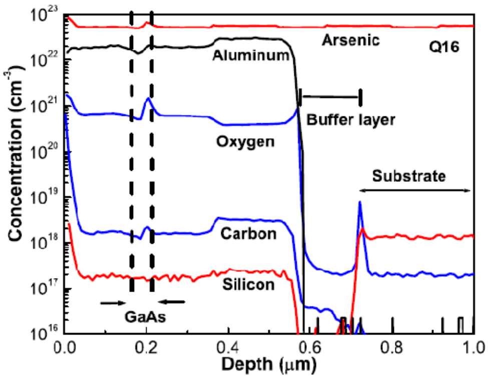

Fig. 7.Profile of concentration of residual impurities in the sample Q16 measured by SIMS. The variations of aluminium concentration during the growth do not result in the increase of oxygen.

Figure 7 illustrates the SIMS profiles of residual impurities of typical sample. Composition profiles show high oxygen content in the samples and the difference in the oxygen concentration between the GaAs buffer layer and the $Al_xGa_{1-x}As$ epitaxial films is of 2 to 3 orders of magnitude. The behaviour of oxygen for the samples presents an abrupt change in the limit region between the GaAs and $Al_xGa_{1-x}As$ layers. This change is related to the time at which the TMAl is introduced to the growth chamber to initiate the growth of the $Al_xGa_{1-x}As$ layer, in such a way that the oxygen presence is directly related to the aluminium source. The oxygen origin is related to the presence of alcohoxides like residual impurities in TMAl. As is observed in Fig. 7 oxygen indicates a clear tendency to accumulate in the inverted interface $GaAs/Al_xGa_{1-x}As$, this result is very important since oxygen not only produces recombination nonradiative centers in the GaAs and $Al_xGa_{1-x}As$ layers, but will affect the structural characteristics of the interface, deteriorating in consequence its optical and electrical properties.

IV. CONCLUSIONS

In this work, we report the successful growth of AlGaAs epitaxial layers using a modified MOCVD system and solid arsenic as precursor. The samples presented photoluminescence signal and a good homogeneity measured by Raman spectroscopy. In the experiments, a wide range of parameters were explored but the samples, in general, showed a hazy surface and high roughness. These characteristics can be associated with the processes of decomposition, diffusion, incorporation, elimination of byproducts and in general to the modified growth kinetics, due to the use of solid arsenic.

We have studied Raman scattering of $Al_xGa_{1-x}As$ films grown by MOCVD at several growth temperatures from 650°C to 800ºC using solid arsenic as arsenic source. The best samples were grown at around 750ºC, for samples grown at lower or higher temperatures some forbidden Raman signals were observed. Those prohibited signals can be provoked by the resulting high concentration of the residual impurities.

The Al composition in the ternary alloy was determined using the peak frequency of the LO like modes. The small shoulder on the low-frequency side of the GaAs-like LO phonon is the GaAs-like TO mode, in principle forbidden in the experimental geometry, can be assigned to the high residual impurity of the AlGaAs layers. Its appearance suggests that the crystal quality of the AlGaAs layers grown by MOCVD using elemental arsenic is not perfect, but its small intensity indicates that the quality is good.

The samples grown by MOCVD using elemental arsenic were highly doped with oxygen, carbon and silicon. The origin of the impurities is related to the chemical grade of the organometallic sources. We obtained, by Hall effect, free carrier concentration about $1.7x10^{16}$-$4.2x10^{17}$ cm^{-3}, but lowmobility, meaning that the samples are highly compensated. These obtained results are compared with the reported ones in the literature.

REFERENCES

[1] Properties of III-V Quantum Wells and Superlattices. Ed, P. Bhattacharya. INSPEC, 1996.

[2] G. B. Stringfellow "Organometallic Vapor Phase Epitaxy :Theory and Practice", Academic Press, Inc. Harcourt Brace Jovanovich, Publishers, 1989.

[3] Shirley S. Chu, T. L. Chu, R. F. Green, and C. Cerny, "Epitaxial growth of GaAs films from elemental arsenic". J. Appl. Phys. **69** (1991) 8316-8319.

[4] R. Peña-Sierra, J. G. Castro-Zavala, A. Escobosa, "Growth of GaAs by MOCVD using a solid arsenic source". J. Cryst. Growth **107** (1991) 337-341.

[5] ASTM Standard test Methods for Measuring Resistivity and Hall Coefficient and Determining Hall Mobility a Single-Crystal Semiconductors. ASTM, F76-86, Oct. 31, 1986.

[6] T. F. Kuech, R. Potemski, F. Cardone, G. Scilla, "Quantitative Oxygen Measurements in OMVPE $Al_xGa_{1-x}As$ Grown by Methyl Precursors". J. Electron. Mater. **21** (1992) 341-346.

[7] G. Wicks, W. I. Wang, C. E. C. Wood, L. F. Easstman, L. Rathbun, "Photoluminescence of $Al_xGa_{1-x}As$ grown by molecular beam epitaxy". J. Appl. Phys. **52** (1981) 5792-5796.

[8] M. Mashita, H. Ishikawa, T. Izumiya, "Comparative study on carbon incorporation in MOCVD AlGaAs layers between arsine and tertiarybutylarsine". J. Cryst. Growth **155**(1995) 164-170.

[9] M. Miyashita, H. Kizuki, M. Tsugami, N. Fujii, Y. Mihashi, S. Takamiya, "Metalorganic chemical vapor deposition growth of high-quality AlGaAs using dimethylethylamine alane and triethylgallium–dimethylethylamine adduct". J. Cryst. Growth **192** (1998) 79-83.

[10] Y. Shiraki, T. Mishima, M Morioka, "Low temperature MBE growth of high quality AlGaAs". J. Cryst. Growth **81** (1987) 164-168.

[11] T. F. Kuech, E. Veuhoff, "Mechanism of carbon incorporation in MOCVD GaAs". J. Cryst. Growth **68** (1984) 148-156.

[12] T. Nakanisi,"The growth and characterization of high quality MOVPE GaAs and GaAlAs". J. Cryst. Growth **68** (1984) 282-294.

[13] P. K. Bhattacharya, T. Matsumoto, S. Subramanian, "The relation of dominant deep levels in MOCVD $Al_xGa_{1-x}As$ with growth conditions". J. Cryst. Growth **68** (1984) 301-304.

[14] Z. R. Wasilewski, M. N. Dion, D. J. Lockwood, P. Poole, R.W. Streater, A. J. Spring-Thorpe, "Composition of AlGaAs". J. Appl. Phys. **81**(1997) 1683-1694.