

Raman and Hall characterization of AlGaAs epilayers grown by MOCVD using elemental arsenic

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MOCVD AlGaAs thin films were characterized using Raman and Hall measurements. The AlGaAs thin films were grown by MOCVD using metallic arsenic instead of arsine as the arsenic precursor. Some difficulties in the growth of AlGaAs by MOCVD are the composition homogeneity of the layers and the oxygen and carbon incorporation during the growth process. The composition homogeneity of the films was demonstrated by the Raman measurements. Hall measurements on the samples showed highly compensated material. Samples grown at temperatures lower than 750°C were highly resistive. Independently of the V/III ratio; the samples grown at higher temperatures were n-type. As the growth temperature is increased the layers compensation decreases but the Raman spectra show the layers become more defective.

Keywords: Raman Spectroscopy; Hall Effect; AlGaAs; MOCVD

1. Introduction

GaAs/AlGaAs heterojunctions are the fundamental elements for most optoelectronic devices such as: semiconductor lasers, photodetectors, wave-guide optical modulators, solar cells, etc. The crystalline quality of the semiconductor epitaxial layers forming such heterojunctions and their interfacial quality are crucial parameters in the device performance [1]. Even when the GaAs and AlGaAs have been extensively studied in the past, nowadays there are under research new applications of these semiconductors in novel forms such as nanocrystallites, quantum wires (QW) and dots (QD), etc. These new applications fields were feasible due to the use of MOCVD and MBE growth techniques, which provides very precise control of layer thickness on the range of subnanometric dimensions [2]. However, for those applications we require a better and deeper understanding on the basic properties of these materials and on the optimization of their characteristics in terms of the involved growth parameters.

The growth of AlGaAs by MOCVD presents different problems such as the difficulty for growing at low temperatures. Of special importance is the growing for temperatures under 600 °C because of the QD are usually grown around this condition. For low temperatures the poor arsine decomposition limits the growth process therefore the growth systems must include an additional arsine pre-cracking stage. Of the uppermost importance is the control of undesirable impurities in MOCVD Al_xGa_{1-x}As such as oxygen and carbon [3]. When the Aluminum concentration in Al_xGa_{1-x}As reaches or increases above the limit of the indirect band gap region the role of the residual impurities becomes very sensible to the growth conditions.

To solve these problems several attempts have been made for replacing arsine in growing GaAs and its alloys by

MOCVD, precursors such as trimethylarsenic, triethylarsenic and solid arsenic have been used [4]. When trimethyl- or triethylarsenic are used the GaAs layers have resulted with high background doping and high compensation rate, due to the incorporation of carbon doping coming from the organic radicals [5]. When growing Al_xGa_{1-x}As the problem becomes more complex due to the chemical affinity between aluminum and carbon, furthermore the batches of metallorganic precursors possess oxygen which could degrade definitely the properties of the epilayers [6].

The main interest of the work is the development of GaAs and Al_xGa_{1-x}As epitaxial layers for applications on current quantum well technology [3]. In this work we report the structural and electrical characterization of Al_xGa_{1-x}As epilayers grown by the MOCVD technique based on a solid arsenic source [7]. The use of the solid arsenic source can be feasible the growth of Al_xGa_{1-x}As epilayers at temperatures lower than 600°C and precludes the use of dangerous arsine as arsenic precursor [7]. However, the use of non-arsine precursors as arsenic precursor produces low quality AlGaAs epilayers due to the oxygen and carbon incorporation [8]. Therefore our study will be directed in analyzing the influence of the use of metallic arsenic on the electrical and structural properties in growing Al_xGa_{1-x}As epilayers.

2. Experimental details

The used MOCVD system operates at atmospheric pressure; the details of the MOCVD growth system were published elsewhere [7]. The arsenic vapor from a solid arsenic source is transported by diffusion until the growth zone; other authors use a hydrogen flow through an additional oven containing arsenic in order to transport it to the sample surface. The arsenic pressure is controlled

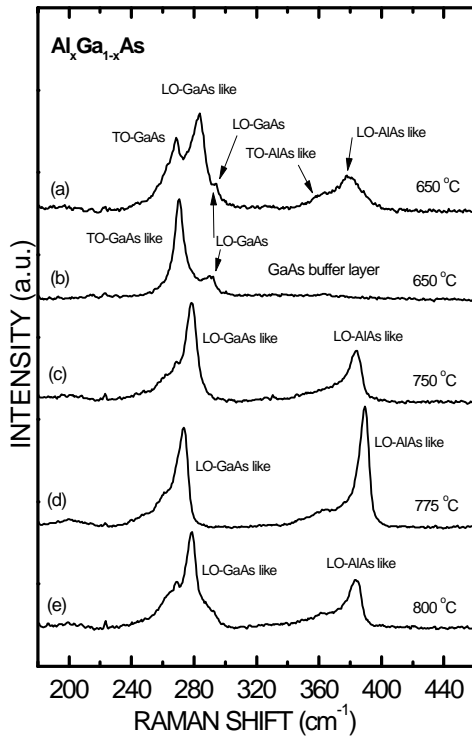


Figure 1. Raman spectra for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers grown at several temperatures by MOCVD using metallic arsenic. The Al composition values calculated using the eqs. (1) and (2) are: $x=0.19$ (a), $x=0.32$ (c), e) and $x=0.46$ (d).

independently by a second oven for better control of the process [4]. In our case the arsenic source is self-contained and the reactor walls do not need to be heated along to prevent arsenic condensation [4]. The gallium and aluminum precursors were trimethylgallium (TMG) and trimethylaluminum (TMA), respectively. For preventing the pre-cracking of the metallorganic precursors the path was maintained cold as is usual in conventional MOCVD. The flow of TMG was fixed in the range of 0.8 $\mu\text{mol}/\text{min}$ to 2.2 $\mu\text{mol}/\text{min}$, and the flow of TMA was in the range 0.8 $\mu\text{mol}/\text{min}$ to 2.2 $\mu\text{mol}/\text{min}$. The arsenic flux was varied between 7.0 $\mu\text{mol}/\text{min}$ to 15.0 $\mu\text{mol}/\text{min}$ by controlling the arsenic temperature (T_{As}) of the arsenic source between 550 and 580 °C.

Some experiments were carried out to determine the highest temperature that could be supported by TMG without being decomposed, since partial cracking of trimethylgallium can lead to the building of gallium droplet or GaAs nuclei, which could produce morphology defects, faceted growth and, in extreme cases, polycrystalline epilayers [7].

The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epitaxial layers were grown on semi-insulating (100)-oriented GaAs single crystals. Previous to the growth of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epitaxial layers in all the cases a high quality GaAs buffer layer of 0.1 μm was grown at 650°C. The used growth temperatures (T_{C}) were in the range of 650 to 850 °C. For studying the AlGaAs layers composition and their homogeneity Raman measurements were made on the growth samples. Raman

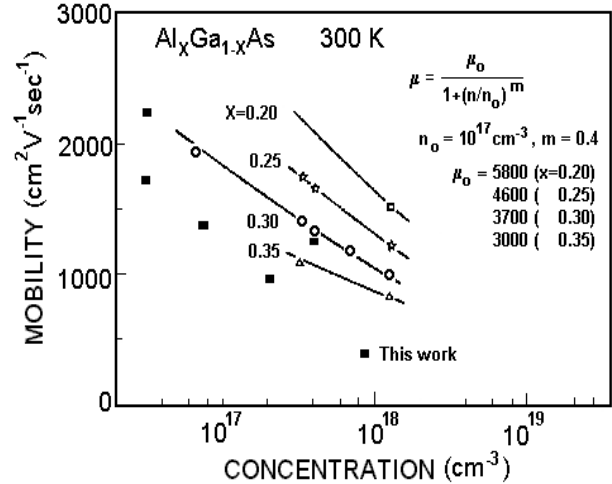


Figure 2. The electron mobility as a function of the free carrier concentration in MOCVD $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers

scattering experiments were performed at room temperature using the 5145 Å line of an Ar laser at normal incidence for excitation. The light was focused to a diameter of 6 μm at 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 analyzed using a Jobin-Yvon T64000 triple spectrometer, operating in the subtractive configuration, and a multichannel charge-coupled device detector cooled to 140 K using liquid nitrogen. Typical spectrum acquisition time was limited to 60 s to minimize the sample heating effects discussed above. Absolute spectral feature position calibration to better than 0.5 cm^{-1} was performed using the observed position of the Ar-ion laser plasma line 34 (5287 Å) which is red-shifted by 521.2 cm^{-1} from the excitation line.

The electrical properties of the samples 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 corners of the samples, for alloying the contacts to surface sample, these were annealed at a temperature of 400°C for 1 min in an atmosphere of nitrogen. The linearity and symmetry of the ohmic contacts were tested following the procedure described in the ASTM standards [9].

3. Results and discussion

The surface characteristics of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epitaxial layers were very sensible to the growth temperature. At low temperatures mirror like surfaces were obtained, as the growth temperatures (T_{C}) reached 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 as the substrate temperature is increased. For temperatures greater than 800°C the surface appeared hazy and in some cases eventually becomes polycrystalline as was examined by X-ray measurements [10].

Figure 1 shows Raman scattering results of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers grown by MOCVD at several temperatures of growth (T_C) using metallic arsenic. In the same figure the Raman spectra for a GaAs epilayer (spectra (b)) is included, the corresponding layer was grown at the same growth conditions that were used for the GaAs buffer layers. In the spectrum the TO and LO GaAs modes at 268 and 292 cm^{-1} , respectively, are clearly distinguishable. In the spectrum (a), the signals at 283.4, 363.2 and 378.7 cm^{-1} assigned to 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers, the modes corresponding to GaAs should not be assigned to the buffer layer. A possible explanation of the presence of the GaAs-like signals, is the possible existence of crystalline defects in the epitaxial layers. The prohibited signals are more clearly observed for samples grown at the extreme growth conditions. The Al composition for the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples can be determined using the fitted curves that relate the LO-phonon frequency with the aluminum content in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system, according to the next equations [11]:

$$\omega_{LO}^{GaAs}(x) = 290.2 - 36.7x \text{ cm}^{-1} \quad (1)$$

$$\omega_{LO}^{AlAs}(x) = 364.7 + 46.7x - 9.4x^2 \text{ cm}^{-1} \quad (2)$$

We can find the Al composition of the ternary films. For the same spectrum (a) and according to the LO-GaAs like and LO-AlAs like peak position we found $x \sim 0.19$. As was mentioned before, the spectrum corresponding to a GaAs epilayer, only the LO and TO modes for GaAs are visible. For the spectra corresponding to the samples grown at $T_C = 750, 775$ and 800°C (c, d, and e, respectively), the LO-GaAs like and TO-GaAs like modes appear as a small contributions of the principal. The calculated Al compositions for those samples were; $x \sim 0.32$ for $T_C = 750^\circ\text{C}$, $x \sim 0.46$ for $T_C = 775^\circ\text{C}$ and $x \sim 0.32$ for $T_C = 800^\circ\text{C}$. Thus, we find a homogeneous behavior of the Raman signals of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ films for growth temperatures above to 750°C , whereas for growth temperatures below 750°C the signals arising from the buffer GaAs layer have an important contribution to the total spectrum. 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. Its appearance indicates that the crystal quality of the AlGaAs layers is not perfect, but its small intensity indicates that the quality is good. It suggests that the crystal quality of the AlGaAs epilayers degrades either when the

growth temperature was lower than 650°C or was increased above 800°C .

According to the electrical characteristics of the epilayers, they can be grouped in two ranges of growth temperatures. The first group is constituted by samples grown at temperatures in the range of 650 to 750°C , these samples resulted highly resistive and their electrical characterization was difficult. The second group is formed by samples grown at temperatures greater than 750°C , those samples resulted n-type with a free carrier concentration around $10^{16} - 10^{17} \text{ cm}^{-3}$.

Some results of the electrical characterization are presented in the table I, in the same table are also included some of the relevant growth conditions. In spite of the epilayers were grown without intentional doping, however, a great amount of the incorporated residual impurities to the layers come from of 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^{18} , and $10^{16} - 10^{17} \text{ cm}^{-3}$, respectively [10].

The measured electron concentration range is approximately from 10^{16} cm^{-3} up to 10^{17} cm^{-3} . As the growth temperature was increased the carrier concentration only registered a slight increment. The Hall measurements at 77 K shown the 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers could increase at levels greater than 10^{19} cm^{-3} [16]. From the results presented in the table I, we may note some important facts. The electron mobility at 300K for the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers grown with metallic arsenic is comparable to the mobility of the samples grown in arsine based MOCVD systems [12,13,14]. In the Fig. 2, we compare the free carrier mobility of our samples with those grown by conventional MOCVD systems [15]. The differences between the measured carrier concentration with those taken from the reference [15], can be related to the presence of carbon and oxygen as compensating 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} . Therefore the measured carrier mobility is strongly influenced by the total impurity concentration in the epilayers.

With reference to the role of the arsenic source in the epilayer characteristics, the changes on the arsenic pressure apparently do not influence the electrical properties of the samples. As can be seen in the 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 $2500 \text{ cm}^2/\text{Vsec}$, these values are in range with those reported by other authors for arsine based MOCVD process.

Table 1. Electric measurements obtained by Hall effect of Al_xGa_{1-x}As layers grown by MOCVD. The table contains the thermodynamic parameters of growth.

Sample	T _C (°C)	T _{As} (°C)	Flow (μmol/min)	Thickness (μm)	N ₃₀₀ (cm ⁻³)	μ ₃₀₀ (cm ² /V*s)	N ₇₇ (cm ⁻³)	μ ₇₇ (cm ² /V*s)	Resistivity (Ω-cm)
1169	750	570	-----	2.48	1.34x10 ¹⁷	538	2.30x10 ¹⁷	1265	0.086
258	750	570	-----	2.48	2.33x10 ¹⁶	876	1.68x10 ¹⁷	1023	0.03
1235	800	570	9.0	0.83	2.20x10 ¹⁷	943	2.30x10 ¹⁷	1265	0.02
126	820	585	15.0	0.91	1.40x10 ¹⁶	1718	5.60x10 ¹⁵	1807	0.03
1173	850	570	9.0	2.98	4.20x10 ¹⁷	1272	3.90x10 ¹⁷	1173	0.01
57	870	570	9.0	0.48	1.70x10 ¹⁶	2290	1.68x10 ¹⁶	2921	0.06
Q39	875	565	7.0	0.5	7.30x10 ¹⁶	1421	8.68x10 ¹⁶	3212	0.06

These experimental results indicate that we can grow Al_xGa_{1-x}As epilayers using elemental arsenic by MOCVD, which may be used to make optoelectronic devices.

4. Conclusions

We have studied Raman scattering of Al_xGa_{1-x}As films grown by MOCVD at several growth temperatures from 650°C to 800°C using solid arsenic as arsenic source. The best samples were grown at around 750 °C, for samples grown at lower or higher temperatures some prohibited 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 1.7x10¹⁶-4.2x10¹⁷ cm⁻³, but mobility low, meaning that the samples are highly compensated. These obtained results are compared with the reported ones in the literature.

Acknowledgement

The authors would like to acknowledge M. Rojas-López for the useful discussions on Raman and for having made the Raman measurements.

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