Optical and electrical characterization of Al$_x$Ga$_{1-x}$As layers grown on GaAs obtained by a metallic-arsenic-based-MOCVD system

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In this work we report results on the optical characterization of Al$_x$Ga$_{1-x}$As epitaxial layers. The layers were characterized using photoluminescence (PL) to 10 K and photoreflectance (PR) to 300 K. The Al$_x$Ga$_{1-x}$As layers resulted n-type with an electron concentration of $1 \times 10^{17}$ cm$^{-3}$ and a corresponding carrier mobility of about 2200 cm$^2$/N*s. The studies of the chemical composition by SIMS exhibit the presence of silicon, carbon and oxygen as the main residual impurities. The silicon concentration of around $1 \times 10^{17}$ cm$^{-3}$ is very close to the carrier concentration determined by the Hall-van der Pauw measurements. The 10 K photoluminescence response of the samples is strongly dependent on the growth temperature. Growth temperatures higher than 750°C were necessary to detect a reasonable photoluminescence signal. The residual oxygen detected on the samples could be responsible for the weak photoluminescence signal. Photoreflectance spectra present two transitions mainly associated to GaAs and Al$_x$Ga$_{1-x}$As. In addition, short period oscillations near the GaAs band-gap energy are observed, and are interpreted as Franz-Keldysh oscillations associated to the hole-ionized acceptor (h-A$^-$) pair modulations. Using the Al$_x$Ga$_{1-x}$As band-gap obtained by PR, we calculated the molar fraction of aluminum, giving $x = 0.221$ of molar fraction.

Keywords: Semiconductors growth; Al$_x$Ga$_{1-x}$As; MOCVD; photoluminescence; photoreflectance.

En este trabajo presentamos los resultados de la caracterización óptica de capas epitaxiales de Al$_x$Ga$_{1-x}$As. Las capas fueron caracterizadas usando fotoluminiscencia (FL) a 10 K y fotoreflectancia (FR) a 300 K. Las capas de Al$_x$Ga$_{1-x}$As resultaron n-type con una concentración de electrones de $1 \times 10^{17}$ cm$^{-3}$ y una movilidad de portadores correspondiente de aproximadamente de 2200 cm$^2$/N*s. Los estudios de la composición química por SIMS exhiben la presencia de silicio, carbón y oxígeno como las principales impurezas residuales. La concentración de silicio alrededor de $1 \times 10^{17}$ cm$^{-3}$, está muy cerca de la concentración de portadores determinada por medidas de Hall-van der Pauw. La respuesta de fotoluminiscencia a 10 K de las muestras es fuertemente dependiente en la temperatura del crecimiento. Temperaturas de crecimiento más altas que 750°C fueron necesarias para detectar una señal de fotoluminiscencia razonable. El oxígeno residual detectado en las muestras podría ser el responsable de la débil señal de fotoluminiscencia. Los espectros de fotoreflectancia presentan dos transiciones principales asociadas al GaAs y al Al$_x$Ga$_{1-x}$As. Además, oscilaciones de período corto cerca de la energía de la banda prohibida del GaAs son observadas, interpretadas como oscilaciones de Franz-Keldysh asociadas a las modulaciones por hueco-aceptor ionizado (h-A$^-$). Usando el ancho de banda prohibido del Al$_x$Ga$_{1-x}$As obtenido por FR calculamos la fracción molar del aluminio, dando $x = 0.221$ de fracción molar.

Descripores: Crecimiento de semiconductores; Al$_x$Ga$_{1-x}$As; MOCVD; fotoluminiscencia; fotoreflectancia

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1. Introduction

One of the premises for the production of optoelectronic devices is, without a doubt, the preparation of materials with sufficient quality for fabricating them with the desired characteristics. The Al$_x$Ga$_{1-x}$As/GaAs system has demonstrated to be one of the more useful ones for its great variety of applications. The structures with epitaxial layers of these materials are used in laser diodes, magnetic field detectors, high mobility transistors and modern devices with superlattices, etc.

The growth of epitaxial layers by Metal Organic Chemical Vapor Deposition (MOCVD) presents difficulties for the great chemical reactivity of aluminum. Aluminum strongly bonds with oxygen, favoring its incorporation during the growth processes. Oxygen introduces no-radiative recombination centers, which degrade the optical properties of Al$_x$Ga$_{1-x}$As. Another equally noxious impurity is carbon, which affects the carrier mobility. Due to this, the identification of the sources that introduce these impurities in the growth processes as well as the control of their concentration to low levels is very important. The quality of the material strongly affects the device characteristics, such as luminescence efficiency and carrier concentration. It has been shown that Al$_x$Ga$_{1-x}$As grown using the organometallic va-
por phase epitaxy (OMVPE) technique contains a significant amount of residual impurities, such as oxygen and carbon, especially for large AlAs $x$ mole fraction. The electronic properties of Al$_x$Ga$_{1-x}$As are strongly affected by these impurities, particularly for undoped material; for example, oxygen creates deep traps [1] and leads to a decrease in carrier mobility. On the other hand, carbon is a well-known shallow acceptor, which determines the background carrier concentration [2]. Reducing or controlling the O and C concentrations is the key problem in the realization of the high-performance electron devices [3], and for this reason, understanding the effects of these two residual impurities is important.

In this work we report the results of the optical and electrical characterization studies carried out in Al$_x$Ga$_{1-x}$As layers grown by MOCVD, which in order to eliminate the risks by the use of arsine in this process, our system uses a metallic arsenic source. The absence of atomic hydrogen that would give the arsine during its decomposition, as it occurs in the conventional systems, produces peculiar characteristics in the layers, as will see more below.

2. Experimental details

The Al$_x$Ga$_{1-x}$As layers were grown in an MOCVD system at atmospheric pressure; its characteristics have been reported in the literature [4]. The substrates were (100) GaAs semi-insulating doped with Chromium, or of n-type conductivity doped with silicon. The precursors of gallium and aluminum were trimethylgallium (TMG) and trimethylaluminum (TMAI), respectively; and the arsenic used was metallic arsenic of 7N [4]. The flux of transporting hydrogen was of 3 slpm, and the flux of TMG was of 7.0 $\times$ 10$^{-6}$ mol/min. The ratio V/III was higher than 12. It fixed the temperature of TMAI and its flux for obtaining Al$_x$Ga$_{1-x}$As layers with $x = 0.25$ molar fraction. It explored the range of growth temperatures ($T_G$) of 650 to 950°C.

To obtain the photoluminescence measurements (PL), we used a monochromator of double grating trademark SPEX model 1406, and an amplifier lock-in PAR 124. As an exciting source, we used a He-Ne laser ($\lambda = 632.8$ nm) with 20 mW. The PL measurements at 10 K were made with a cryostat of closed cycle of Helium. The PR spectra were obtained at room temperature in an automatized system as described in Ref. 5. The 488nm-line of argon-ion laser was used as the modulated and exciting light source, with a nominal power density of 15 mW/cm$^2$, chopped at a frequency of 108 Hz. Reflected light was detected with a Si photodiode, whose output was fed into a lock-in amplifier.

3. Results and discussion

For the growth temperature ($T_G$) range from 650 to 800°C, the layers presented a better surface morphology. For temperatures higher than 850°C defects were manifested by homogeneous nucleation. For growth temperatures of 650 to 750°C, the samples presented high resistivity, impeding the formation of ohmic contacts and therefore their electrical characterization. The conductivity of the layers increased when $T_G$ increased, and their conductivity was always n-type. The high resistivity that was obtained at samples grown at temperatures lower than 750°C seems to be related to the presence of oxygen as residual impurity [6,7], a hypothesis that corroborates with the obtained results of chemical composition characterization by SIMS [4]. Of course, to different authors [6,8], oxygen in Al$_x$Ga$_{1-x}$As introduces energy levels that act as dispersion centers, and reduces the electrical conductivity. Taking as reference one $T_G$ can advise a slight increase in the electron mobility when the temperature increases. This behaviour agrees with the decrease in the incorporation of oxygen to increase the growth temperature [9,7]. It is important to emphasize that an increase in the growth temperature usually increases the vacancy concentration of arsenic, and in general, increases the crystalline defects deteriorating the crystalline quality of the layers. As a result, important effects were not observed to increase the partial pressure of arsenic during the growth process. The apparent insensitivity to the relation V/III would be due to the relative high donor residual concentration which is manifested in the samples. In the processes with arsine, utilize very high ratios V/III by the low efficiency of crack of the arsine. In our case, even when the ratio V/III seems low, the present specie is As$_4$ and the unique intermediate process for its incorporation to the lattice is its decomposition to atomic arsenic. Some authors have demonstrated that the Al$_x$Ga$_{1-x}$As grown by MOCVD in a rich atmosphere in arsenic, as apparently occurs in our system, diminishes the impurity concentration because of the reduction in the surface mobility of the Ga and Al. Other authors have demonstrated that rough surfaces form in these conditions [2,8]. According to the electrical characteristics of the epilayers, they can be grouped into 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 $10^{16} - 10^{17}$ cm$^{-3}$.

According to the electrical measurements, the Al$_x$Ga$_{1-x}$As layers grown in lower temperatures than 750°C present a very weak PL signal, Fig. 1. Similar results have been reported for layers grown by MOCVD or MBE. The behavior relates to the presence of no-radiatives recombination centers due to residual impurities, in particular to oxygen [10]. In the growth system that we utilized, it is observed that to obtain a noticeable signal of PL, the minimum growth temperature should be higher than 780°C, independently of the value of $x$. In conventional MOCVD systems, a critical temperature of $T_G \approx 580°C$ is indicated [11]. In this case, it should be mentioned that because of the arsenic source used, a greater carbon concentration in the layers would be expected due to a lack of atomic hydrogen. The carbon like
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Figure 1. Low-temperature Photoluminescence spectra of Al$_x$Ga$_{1-x}$As layers. In samples (a) and (b) the growth temperatures vary, while the arsenic temperature remains constant. In figures (a) and (c) the arsenic temperatures vary, while the growth temperature is constant.

Figure 2. Concentration profiles of residual impurities in a typical sample measured by SIMS.

acceptor impurity compensates to the n-type Al$_{1-x}$Ga$_x$As layers. The total carbon concentration may overtake up to 10$^{18}$ cm$^{-3}$ as has been found by SIMS [4], Fig. 2. When one utilized growth temperatures higher than 800°C, the PL signal notably improved. The epitaxial layers with the better PL characteristics were obtained at the growth temperatures range of 850 to 900°C. At growth temperatures near 950°C, an increase in the surface defect density of the layers observed, and at temperatures higher than 970°C, some layers turned polycrystalline due to problems of nucleation in the homogeneous phase [12].

Figure 1 illustrates PL spectra obtained in three typical samples; in them, one can observe light shifts to vary the more important experimental parameters, as are the growth temperature and the arsenic source temperature. In PL spectra, one can appreciate that PL signals corresponding to Al$_x$Ga$_{1-x}$As layers have a very large full width high maximum (FWHM). At a first approximation, the characteristics of these signals allow one to associate them to donor-acceptor transitions, and the FWHM value can be related to the level of carrier concentration in the layers. The signals sited at 1.514 and 1.4185 eV come from the GaAs buffer layer and correspond to band edge and band-acceptor impurities transitions, respectively. The intensity of the PL signals of Al$_x$Ga$_{1-x}$As layers is appreciably lower than those that arise from buffer layer.

To consider a single arsenic temperature (ratio V/III constant), observe that an increased light of the growth temperature has an influence in a determinant way in the PL signal intensity, as it is indicated in the PL spectra of Figs. 1a and 1b. In these layers, with an experimental estimated concentration of aluminum of $x = 0.25$, the PL intensity increased by a factor of 5 for an increase in the growth temperature of 25°C; a higher growth temperature improves the signal intensity. In both cases, the FWHM values are similar ($\approx 100$ meV); this indicates that the impurity concentration does not vary notably. Figure 1c includes a PL spectrum for a layer grown in similar conditions, $T_G = 850°C$. The measured concentration of aluminum was estimated to be about $x = 0.14$; the difference with the expected value of $x = 0.25$ could be due to possible variations in the flux in the growth system. In this sample, the FWHM is about 70 meV. If the value of the FWHM would associate directly to the impurity concentration, its decrease could implicate a reduction in its concentration. Since the main difference between this sample and the earlier ones is the aluminum concentration, one can suggest that the value of the FWHM is related to both the residual impurity concentration and to the aluminum content. It has been demonstrated that a correlation between the aluminum concentration and the concentration of the DX levels in Al$_x$Ga$_{1-x}$As grown by MOCVD exists, especially when the donor level corresponds to silicon. Another characteristic of the PL signals is that it does not manifest excitonic signals as it occurs in non-compensated samples. The values for the FWHM signal of Al$_x$Ga$_{1-x}$As indicate an important influence of the recombination centers associated to residual impurity and centers of characteristic defects of the ternary alloy.

Photoreflectance spectroscopy was applied to the investigation of Al$_x$Ga$_{1-x}$As epilayers. Figure 3 shows the PR spectrum of the Al$_x$Ga$_{1-x}$As (sample MG279). The oscillations...
AlGaAs layers utilizing a MOCVD system to base-metallic–arsenic have been grown. n-type samples with a concentration of \( \sim 10^{17} \text{cm}^{-3} \) were obtained. In general, the measured characteristics are compared with the ones obtained in conventional MOCVD systems, which is a significant result since the growth system avoids the use of arsine.

In the PL studies, one obtained signals with FWHM with a mean of \( \sim 100 \text{ meV} \), which indicates the presence of high residual doping and high characteristic density of the material.

The measurements by PL and PR corroborated the obtained results by the other characterization techniques, as SIMS and Hall effect. We identified as main residual impurities to silicon, carbon and oxygen typical residual impurities in Al\(_x\)Ga\(_{1-x}\)As/GaAs structures that grow by MOCVD. Each of their concentration levels is similar to those which are measured in conventional systems. The oxygen sources are the residual alcooxides in the TMAl source. The carbon sources are the metallorganic precursors. The silicon and oxygen source is the TMAl. The silicon concentration measured by SIMS corresponds with the carrier concentration measured by Hall Effect, and its origin is the aluminum precursor. The concentration level of oxygen seems be the main factor that influences in the characteristics of the layers.

3.1. Conclusions

Al\(_x\)Ga\(_{1-x}\)As layers utilizing a MOCVD system to base-metallic–arsenic have been grown. n-type samples with a concentration of \( \sim 10^{17} \text{cm}^{-3} \) were obtained. In general, the measured characteristics are compared with the ones obtained in conventional MOCVD systems, which is a significant result since the growth system avoids the use of arsine. In the PL studies, one obtained signals with FWHM with a mean of \( \sim 100 \text{ meV} \), which indicates the presence of high residual doping and high characteristic density of the material.

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