

STRUCTURAL CHARACTERIZATION OF CARBON DOPED GAAS LAYERS GROWN BY MOCVD

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Abstract

Este trabajo presenta la caracterización de películas de GaAs tipo-p en un sistema MOCVD que usa arsénico metálico. El precursor de galio fue trimetilgalio (TMG) y arsénico metálico como fuente de arsénico. La influencia de la impurificación en las propiedades físicas de las capas de GaAs ha sido estudiada por mediciones de fotoluminiscencia (FL) y dispersión Raman. Para impurificar con carbón en el rango de 10^{16} a 10^{20} cm⁻³, fue necesario modificar la actividad del hidrógeno en la atmósfera de crecimiento con el control de una mezcla H₂+N₂, que fue utilizada como gas portador. Las respuestas de PL y dispersión Raman de las muestras son fuertemente dependientes de la temperatura de crecimiento, las cuales fueron investigadas en función de la concentración de portadores. Capas de GaAs calidad dispositivo se han crecido a temperatura de crecimiento en un amplio rango de temperaturas desde 550°C y más arriba. La calidad cristalina obtenida por difracción de rayos X es bastante buena en todo el rango investigado.

Keywords: *Semiconductor compounds III-V, MOCVD, GaAs, photoluminescence, Raman scattering, X-ray diffraction*

Resumen

This work presents the characterization of p-type GaAs layers grown in a metallic-arsenic-based-MOCVD system. The gallium precursor was the compound trimethylgallium (TMG) and elemental arsenic as precursor of arsenic, respectively. The influence of the doping in the physical properties of the GaAs layers has been studied by photoluminescence (PL) and Raman dispersion measurements. In order to dope with carbon in the range of 10^{16} to 10^{20} cm⁻³, it was necessary to modify the activity of hydrogen in the growth atmosphere with the control of a mixture H₂+N₂, which was used like carrying gas. The PL and Raman scattering responses of the samples are strongly dependence of the growth temperature, which were investigated based on the hole concentration. Device quality GaAs layers have been grown in a broad range of growth temperatures. The crystalline quality is enough good in whole the investigated range.

Palabras Claves: *Compuestos semiconductores III-V, MOCVD, GaAs, fotoluminiscencia, dispersión Raman, difracción de rayos X*

1. INTRODUCTION

Recently, the investigation of AlGaAs/GaAs heterojunctions bipolar transistors (HBTs) has accelerated from the viewpoint of high speed digital and analog circuits applications. However, unstable behavior of conventional base dopants such as Be and Zn in operating devices, has introduced serious problems for practical devices applications [1]. For further improvements of in the HBTs reliability, it is necessary to develop a growth technique of GaAs epilayers in the high doping range with stable

dopants. Carbon (C) is a successful alternative base dopant because of its very low diffusion coefficient in GaAs. We have investigated the carbon-doping technique in GaAs and AlGaAs by metal organic chemical vapor deposition (MOCVD) using trimethylgallium (TMG) and elemental arsenic hole concentrations is high as 2×10^{20} and 10^{21} cm⁻³ have been achieved in the case of GaAs and AlGaAs, respectively. These concentrations are necessary for the high frequency performance in the devices as HBTs, in order to decrease the base resistance, i. e., to reduce the resistivity in the base layer.

1. EXPERIMENTAL DETAILS

GaAs was grown in an MOCVD system at atmospheric pressure, its characteristics has been reported in the literature [2]. The growth temperature is obtained by a system consist of 4 halogen lights of 500 Watts and a temperature controller of the type PID. The hydrogen, which is the carrier gas, is purified in situ by diffusion through of a Palladium-Silver (Ag-Pd) cell. The substrates were (100) GaAs semi-insulating doped with chromium, or of n-type conductivity doped with silicon. Previous to growth process, the GaAs substrates were prepared using a normal process of cleanliness. The precursor of gallium was trimethylgallium (TMG), as the arsenic source used metallic arsenic of 7N was used. It was explored the range of growth temperatures (T_G) from 620 to 780°C. The electrical properties of the samples were studied using Hall Effect by the Van der Paw method at 77 and 300 K. 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 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. For the photoluminescence measurements (PL) a double grating monochromator, SPEX model 1406, and a PAR 124 lock-in amplifier, were used. As exciting source used a He-Ar laser ($\lambda = 488$ nm) with 20 mW nominal power. The PL measurements at 10 K were made with a closed cycle of He cryostat.

Raman scattering experiments were performed at room temperature using the 5145 Å line of an Ar-ion laser at normal incidence for excitation. The laser light was introduced into a microscope having a 50x (numerical aperture 0.9) microscope objective. The measurements were done with a laser power of 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 N₂. 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. Hall-van der

Pauw measurements were done using standard equipment.

2. RESULTS AND DISCUSION

In the used MOCVD system, when pure hydrogen was used as carrier gas, GaAs layers of p- or n- type were grown for a wide range of experimental conditions. For a constant flow of hydrogen and a fixed V/III ratio, as the growth temperature (T_G) is increased, the layers change from p-type to n-type at around of 650°C. For the samples studied in this work the GaAs films were grown at a temperatures of $T_G = 680^\circ\text{C}$ and the arsenic source was fixed at $T_{As} = 570^\circ\text{C}$, respectively. By x-Ray the epilayer/substrate lattice mismatch did not exceed the value of 4.0×10^{-4} at room temperature. The epitaxial layers were prepared with abrupt planar homoboundaries, and the GaAs/GaAs homointerface transition layer was about 3-4 ML (about 1.2 nm) thick, that indicatives a good crystalline quality. For these experimental conditions and using pure hydrogen the layers were n-type with a carrier concentration of about 10^{16}cm^{-3} . When the transport gas is replaced by a mixture of H₂+N₂, the layers change to p-type and the hole concentration can be controlled precisely as the N₂ is varied in the mixture. As the percentage diminishes in the carrier gas mixture the growth rate decreases and the hole concentration increases.

The carrier concentration of the layers was found to be dependent on the nitrogen percentage of the carrier gas, going from 10^{16}cm^{-3} for layers grown without nitrogen up to 10^{21}cm^{-3} as its concentration reaches 100%. The Hall mobility falls abruptly as the carrier concentration is raised over 10^{20}cm^{-3} . This mobility behaviour can be related to the reduction of the GaAs lattice constant, as reported by others authors [3], as is observed in the table 1. However, other possibility could be the carbon incorporation or some fragments of organic radicals because of there are not enough hydrogen to complete the reaction. This could be the case for grown layers with less than 2% H₂ in the carrier gas. In this case the values for the carrier mobility are much lower than those of related works.

In the photoluminescence a predominance is observed for the radiative transition through carbon acceptors, specially as the hole concentration increases. When only hydrogen is used as carrier gas, the growth rate of the GaAs layers is determined by the amount of TMG introduced in the

growth zone. For the growth conditions utilized in the work, the growth rate without nitrogen was of $8\mu\text{m/hr}$. As the N_2 was introduced in the carrier gas, a gradual reduction in the growth rate is observed until a value of $\sim 1.5\mu\text{m/hr}$ is reached. This behavior may be explained by a reduction in the cracking efficiency of the TMG molecules in an atmosphere rich in nitrogen. In lack of hydrogen the more probable process for the recombination of methyl radicals, $[\bullet\text{CH}_3]$, of the TMG molecule, is the direct interaction between them. When N_2 is introduced in the reactor, the possibility of recombination between radicals is reduced and therefore a reduction on the cracking efficiency of the TMG molecules. A probable effect of the low cracking efficiency is the reduction in the number of cracked molecules and the consequent decrease in the growth rate.

Therefore, the process described early appear to be related to the increase in the hole concentration of the GaAs films as the percentage of N_2 is increased in the carrier mixture. For the condition of lack of N_2 the lower limit of the hole concentration is about 10^{16}cm^{-3} . As the N_2 is introduced the TMG cracking efficiency is reduced and more species $\text{Ga}(\text{CH}_3)_x$ diffuse towards the GaAs surface. As N_2 is introduced, the recombination of methyl radicals is reduced, the carbon incorporation increases and the hole concentration can be as high as 10^{20}cm^{-3} , see table 1. The high levels reached on the hole concentration are reflected in the low mobility measured values. In papers reporting such high levels of hole concentration, the minimum measured hole mobility values were around $40\text{cm}^2/\text{Vs}$. We have measured values as low as $1.0\text{cm}^2/\text{Vs}$ as the hydrogen was decreased at approximately 2% in the mixture of carrier gas. These so little mobility values may be associated to the crystalline quality of the GaAs. As the hydrogen content was furthermore decreased, in some cases the GaAs films eventually become polycrystalline.

The photoluminescence (PL) measurements were used to follow the evolution of the donor-acceptor transitions. In absence of N_2 , the PL spectra shown two characteristic bands, the one at high energies (1.512 eV) is associated to transitions due to impurity-bound excitons, the second one at lower energies (1.49 eV) is related to donor-acceptor transitions. This lower energy band is closely related to the acceptor levels introduced in GaAs by carbon impurities. For GaAs samples grown with a low hydrogen content carrier gas the PL spectra is

dominated by the signal at 1.49 eV. For samples grown with pure N_2 this transition virtually disappears.

Table I. Electrical measurements on GaAs layers grown by MOCVD.

Sample	T_G ($^{\circ}\text{C}$)	T_{As} ($^{\circ}\text{C}$)	p_{300} (cm^{-3})	μ_{300} ($\text{cm}^2/\text{V}\cdot\text{s}$)
358	630	575	7.80×10^{15}	217
359	630	575	6.72×10^{16}	229
451	680	580	1.03×10^{17}	329
476	680	565	2.60×10^{18}	55
448	680	580	7.59×10^{18}	48
370	750	580	1.13×10^{19}	70
371	750	580	1.92×10^{20}	2

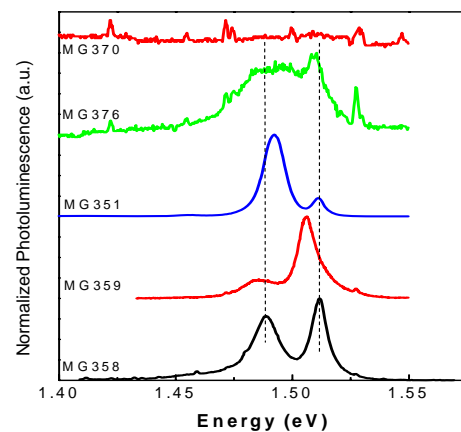


Figure 1. PL spectra of GaAs layers with different hole concentrations.

Figure 2 shows Raman scattering results of GaAs epitaxial films for different values of hole concentration, from 1×10^{17} to $1.5 \times 10^{19}\text{cm}^{-3}$. The first spectrum (line a) corresponds to p-type GaAs film with a hole concentration of $1 \times 10^{17}\text{cm}^{-3}$. It can be observed mainly the presence of the longitudinal optical (LO) mode at 295cm^{-1} . In addition, a small signal at 268cm^{-1} located at the transversal optical (TO) mode position. For the (100) GaAs substrate orientation, the LO mode is allowed and the TO mode is forbidden in the Raman backscattering configuration [4]. The remaining spectra corresponds to GaAs samples with hole concentrations indicated on each curve. The spectrum marked with (b) corresponds to a sample with a hole concentration of $7.4 \times 10^{17}\text{cm}^{-3}$ and, in this case a strong TO-like mode is observed at 268cm^{-1} with intensity comparably to the LO mode. For the remaining samples for carrier concentrations of

3.6×10^{18} and $1.5 \times 10^{19} \text{ cm}^{-3}$, curves (c) and (d), the intensity of the LO mode strongly decreases. The presence of a strong TO-like mode in the highly doped samples is associated with the breakdown of the selection rules [5]. This breakdown is usually attributed to misorientation effects of the growing film produced by markedly increase of carbon concentration [6]. Thus, the appearance of the forbidden TO phonon mode is due to the carbon in the film. The TO-like mode is also has been attributed to elastic scattering by ionized impurities [5].

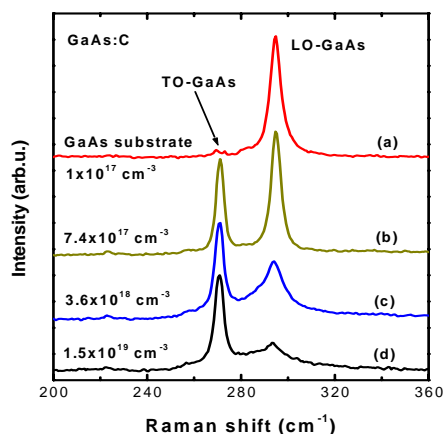


Figure 2. Raman spectra of carbon doped GaAs grown by MOCVD for different carbon concentration levels. It is observed the presence of an intense TO mode.

On the other hand, the LO-mode arises from the fully depletion region of the GaAs epilayers, and the decreasing of the LO-mode intensity is due to the shrinking of the depletion layer as the carbon concentration increases. The influence of the carrier concentration on the LO mode intensity can be explained in the following fashion. The observed Raman spectrum is a superposition of two contributions. The first contribution is originated in the depletion layer near the surface. The widest depletion layer corresponds to the lowest doped samples, therefore in this case an almost pure LO-mode is observed. The LO-mode intensity decreases as the hole concentration increase because the thickness of the depletion layer decreases. The second contribution originates from the whole excited zone as the penetration length remains constant. In this region the interaction of the LO phonon with the collective oscillations of the free-carrier system (plasmons) is carried out. This interaction denoted as LO-phonon plasmon-coupled (LOPC) is due to the macroscopic electric fields associated with both kinds of elementary

excitations. This coupling generates two frequencies (labeled L_+ and L_-) that can be used as a measure of carrier concentration.

For p-type GaAs these LOPC frequencies coincide with the TO- and LO- observed modes and therefore are insensitive to the hole concentration. The larger hole effective mass and lower mobility imply that the plasmon damping effect plays a dominant role in the phonon-plasmon coupling, because this effect can even destroy the collective carrier behavior. Also, this effect downshifts the frequency and broadens the linewidth of the coupled mode for highly carbon doped GaAs [7]. In our case, we have a low and intermediate doping level of carbon in GaAs and we do not observed shift of the LOPC modes. We only observed broadening and decreasing of the intensity of the LO mode with carbon concentration.

3. CONCLUSIONS

The results presented in this work demonstrate the utility of the metallic-arsenic-MOCVD growth process for obtaining C-doped GaAs epitaxial layers. p-type epilayers with hole concentrations as high as 10^{20} cm^{-3} , in a reproducible way and with the peculiarity that no additional doping source is necessary in the MOCVD process. In general the epilayers present mirror-like surfaces. When the hydrogen percentage in the $\text{H}_2\text{-N}_2$ carrier gas mixture was reduced to values less than 2% some degree of polycrystallinity in the films was observed, which may be associated to low mobility of the MO-source cracking products.

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