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Growth and characterization of close-spaced vapor transport GaAs layers, using atomic hydrogen as the initial reactant

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ABSTRACT. The close-spaced vapor transport technique was used to grow a set of GaAs homolayers. The transport agent was atomic hydrogen. The layers were grown leaving fixed all growth parameters except for the spacer thickness δ. Scanning electron microscopy, energy dispersive spectroscopy, and photoluminescence were used to characterize the layers. It is found a phenomenological relationship among the spacer thickness, the growth rate and the surface morphology. The energy dispersive Spectroscopy analysis performed on these layers indicates that all present surfaces with Ga-stabilized structures because of the high temperature effect and the atomic hydrogen interaction with the source and the substrate during the growth processes. By photoluminescence measurements is shown that all samples except for the one with polycrystalline surface morphology have better quality than the substrate, the spectra show a dominant near-gap emission at 1.513 eV at 23.5 K. It is observed also that the near-gap emission of the film grown with the smallest spacer thickness is more efficient. From the performed measurements we conclude that the only contaminant in these layers is carbon.

RESUMEN. La técnica transporte de vapor a corta distancia se empleó para crecer un conjunto de homocapas de GaAs. El agente de transporte fué el hidrógeno atómico. Las capas se crecieron fijando todos los parámetros de crecimiento excepto el grosor del espaciador, δ. Microscopía electrónica de barrido, espectroscopía de energía dispersiva y fotoluminiscencia se emplearon para caracterizar estas capas. Se encontró una relación fenomenológica entre el grosor del espaciador, la razón de crecimiento y la morfología superficial. El análisis de espectroscopía de energía dispersiva efectuado en las capas indica que todas presentan superficies con estructura estabilizada en Ga debido al efecto de alta temperatura y a la interacción de hidrógeno atómico con la fuente y el sustrato durante los procesos de crecimiento. Por medio de las mediciones de fotoluminiscencia se muestra que todas las capas, excepto la de morfología superficial policristalina, tienen mejor calidad que el sustrato, los espectros muestran una emisión cercana a la banda de energía prohibida en 1.513 eV a 23.5 K. Se observa también que esta línea de emisión que presenta la capa crecida con el espaciador de menor espesor es más eficiente. De las mediciones de espectroscopía de energía dispersada y de fotoluminiscencia concluimos que el único contaminante en estas capas es el C.

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1. INTRODUCTION

As is well known, the close-spaced vapor transport (CSVT) [1, 2] is a thin film deposition technique derived from chemical vapor deposition. It has been successfully used to grow a variety of thin films semiconductor materials including homo- and hetero-epitaxial GaAs films [3–5]. The main difference with the other vapor-phase epitaxial (VPE) techniques is that, in the CSVT, the source of the material to be deposited as thin film on the substrate is the material itself. The source and the substrate are located in the reactor and separated by a thin spacer.

In the case of GaAs the transport agent reacts with the source and most likely with the substrate to produce volatile compounds, which then are driven by the source-substrate thermal gradient and deposited on the surface of the substrate. This effect constitutes a net transport of material from the source to the substrate.

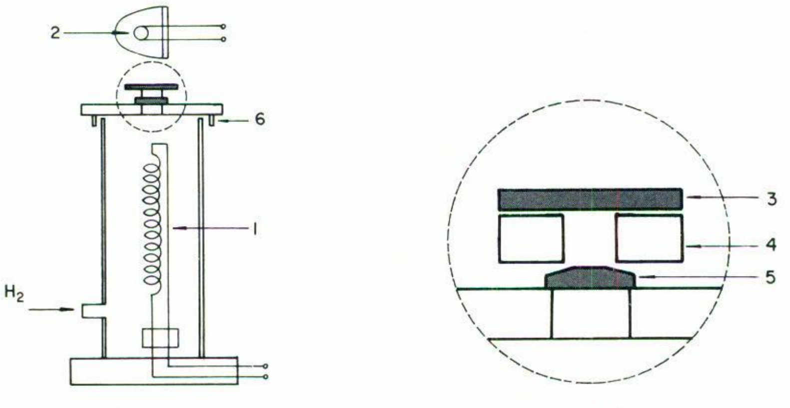
GaAs thin films grown with this technique and water as the transport agent have been extensively investigated and used in the construction of simple structures: as field effect transistors [6], *p-n* junctions [7] and solar cells [8].

Recently using the (CSVT) technique and atomic hydrogen instead of water as the transport agent, GaAs homo-layers have been grown [9]. Later on, the influence of four different experimental CSVT setups in the morphology and elemental composition of GaAs layers grown with this transport agent were analyzed by means of a scanning electron microscope and an energy dispersive spectroscopy system [10].

Naturally, still are many questions about this subject to be answer, some of them are: by what mechanism is the reaction mass transported to the substrate? Is the crystalline quality of the GaAs films so produced, controllable by the growth parameters? In this paper, taking into account the results of our previous work [10], a CSVT system with a new design for the source-substrate assembly is presented. This design is to increase the material transport efficiency. With the modified system and atomic hydrogen as the reactant a set of GaAs layers was grown. In this set the spacer thickness δ was varied while keeping fixed the other growth parameters. Furthermore, the surface morphology and stoichiometry of the as "grown" GaAs layers were analyzed using a JSM-5400LV (JEOL) scanning electron microscope (SEM) in combination with a (Voyager-Noran) energy dispersive X-ray spectrometer (EDS). Finally, the quality of the layers was analyzed by the photoluminescence (PL) technique.

2. EXPERIMENTAL CSVT SETUP

Figure 1 shows a diagram of the CSVT setup used in this work. The elements 1 and 2 are Sylvania tungsten (W) filaments; the former is type EGE, 500 W, 120 V and the latter is ESY, 150 W, and 120 V. The temperature of both filaments are adjusted by independent variable transformers and estimated by their change in resistance with an accuracy of ± 5°C. The filament 1 at temperature T_1, generates the atomic hydrogen [9] and contributes to the formation of the temperature gradient between the source and the substrate necessary in this technique for material chemical transport. The molecular hydrogen flux (f_{H_2}) is carried out into the reaction chamber through the inlet indicated



(a) (b)

FIGURE 1. (a) A scheme of the CSVT system used to grow GaAs layers on GaAs:Cr substrates with atomic hydrogen as the reactant. (b) A magnified view of the source-substrate assembly. 1 and 2 are W-filaments, 3 substrate, 4 a quartz O-Ring, 5 source, and 6 quartz base.

in the figure and measured with a 602 Matheson flowmeter with high accuracy valve orifice with precision of ±1 % of full scale flow rate (±15 scc/min). The filament 2 at temperature T_2 is used to regulate the source-substrate temperature gradient during the deposition time.

The new design of the source-substrate assembly is shown in Fig. 1b. It consists of a quartz plate of $25\times25\times1$ mm^3 with a 6 mm diameter hole in the center. This plate holds the GaAs source. This is of approximately 6 mm × 10 mm × 350 μm, and their 6 mm long edges are cut to a 3.2° bevel angle to provide an inlet-like for volatile compounds to reach the substrate surface. A quartz O-Ring, element 4 in the figure, is located between the source (5) and the substrate (3). It was designed in such a way that its internal wall surrounds the growth zone and its thickness is such that it covers the remaining substrate area. To continue with the terminology used in the literature, the O-Ring height will be denoted by spacer thickness δ. Various spacer thicknesses were used ($\delta = 0.6$, 1 and 2 mm). Additionally, a concentric circle of 0.025 mm depth was etch by photolitography and chemical means on the substrate surface. Only in this particular case, the peripheral step-like was used as the spacer between the source and the substrate instead of a quartz O-Ring.

3. SAMPLES PREPARATION

In this experiment undoped (100) GaAs wafers with $n = 10^{16}$ cm^{-3} were used as sources and Cr-doped semi-insulating GaAs wafers with (100) +2° (110) orientation, $\rho = 10^8$ Ω·cm and EPD = 5–7 × 10^4 cm^{-2} as substrates. Both materials were bought from the MR Semicon Inc. All wafers used were first degreased by the ultrasonic cleaning (2 min. each) in acetone, xylene, acetone, and rinsed in deionized (DI) water. Then, they

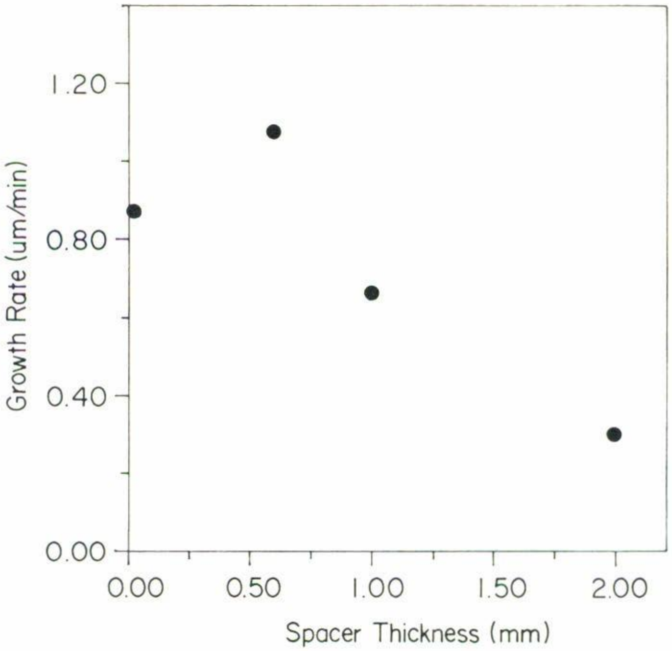
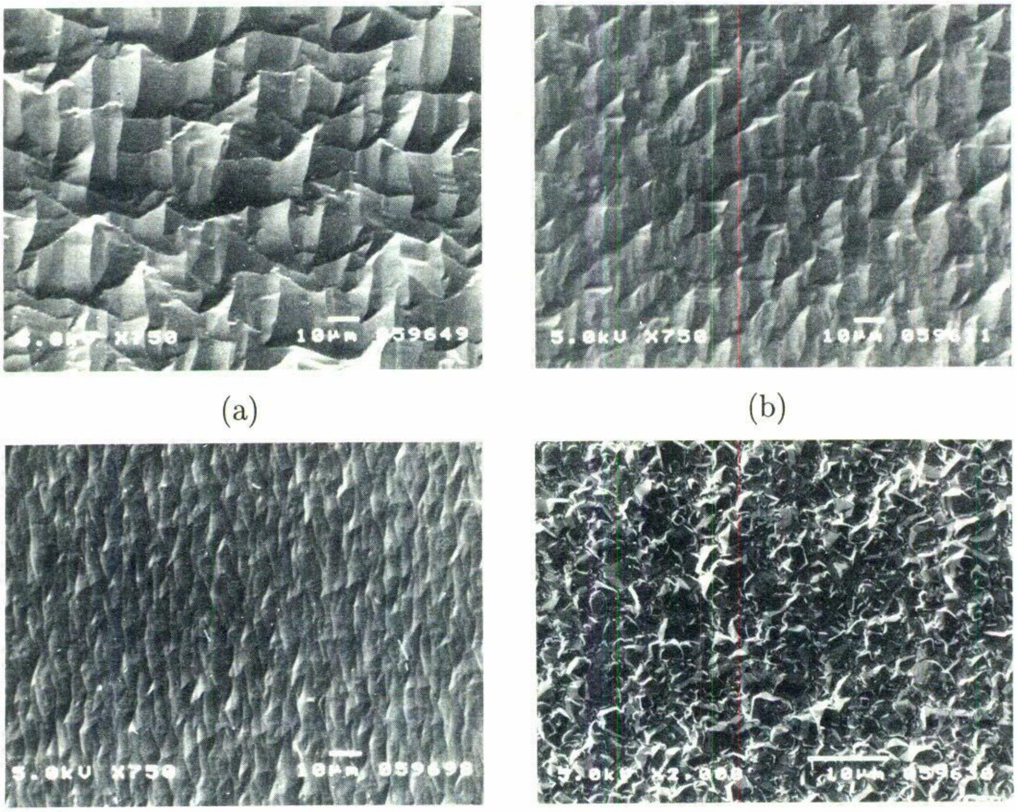


FIGURE 2. Growth rate (GR) *versus* spacer thickness (δ) for CSVT GaAs, with atomic hydrogen as the transport agent.

were etched in 3:1:1 (H_2SO_4:H_2O:H_2O_2) etchant at $T = 80\,^oC$ and finally each sample was dipped into 1:1 (HCl:H_2O) solution to remove residual surface oxides [11], rinsed in DI water and spin-dried just prior introduction into the reaction chamber.

4. RESULTS AND DISCUSSION

First of all, we will mention that during the growth process of the GaAs layers under study, the deposition parameters were kept fixed to: $f_{H_2} = 425$ cm^3/min, $T_1 = 1843^\circ$C, $T_s = 650^\circ$C, and deposition duration $t = 30$ min, while the spacer thickness was varied to $\delta = 0.025$, 0.6, 1, and 2 mm. In the Fig. 2 is shown the variation of the growth rate with the thickness δ for spacer. The growth rate is defined [12] as GR[μm/min]= d[μm]/t[min], where d is the layer thickness. It can be seen, that for $\delta = 0.6$, 1 and 2 mm, the growth rate of the GaAs layers decreases with increasing the source to substrate separation in a similar way as for the GaAs layers grown with H_2O as the transport agent [12]. We would think that for $\delta < 0.6$ mm the GR will increase, however thinking twice, $\delta = 0.025$ mm is a value pretty close to $\delta = 0$, where we expect no growth. Thus, the experimental GR for $\delta = 0.025$ mm is correct, furthermore we suppose that between $\delta = 0.025$ and 0.6 mm there must be a curve with positive slope, reaching a maximum and decreasing until reaching the GR value for $\delta = 0.6$ mm. Unfortunately, the GRs for $\delta < 0.3$ mm are not reported in the literature to compare with.



(a) (b)

(c) (d)

FIGURE 3. Surface morphology (SEM images) of the GaAs layers deposited with a CSVT system, having used spacer with different thickness (δ). (a) with $\delta = 0.025$, (b) $\delta = 0.6$, (c) $\delta = 1$, and (d) with $\delta = 2$ mm.

4.1. SEM STUDY

In Fig. 3 is shown the variation on the surface morphology of the GaAs layers grown with different spacer thicknesses δ, (a) for $\delta = 0.025$, (b) $\delta = 0.6$, (c) $\delta = 1$, and (d) for $\delta = 2$ mm.

It has been reported [13] that, thermodynamic considerations and studies of the initial stages of epitaxy have led to the distinction among 3 different growth modes, which can be adopted by a film growing under (near-) equilibrium conditions. In the Frank-van der Merwe (FM) mode the overlayer grows continuously in a two-dimensional (2D) layer-by-layer way. In the Volmer-Weber (VW) mode nucleation occurs by immediate formation of three-dimensional (3D) islands, and in the Stranski-Krastanov (SK) mode, the initial nucleation occurs in a 2D way but above a certain thickness, t_{SK} island formation occurs. According to the stated above, the first 3 SEM images of Fig. 3 correspond to different (SK) growth modes: in (a) is shown a kind of soft stepped surface, in (b) a piramidal growth and in (c) a wavy texture.

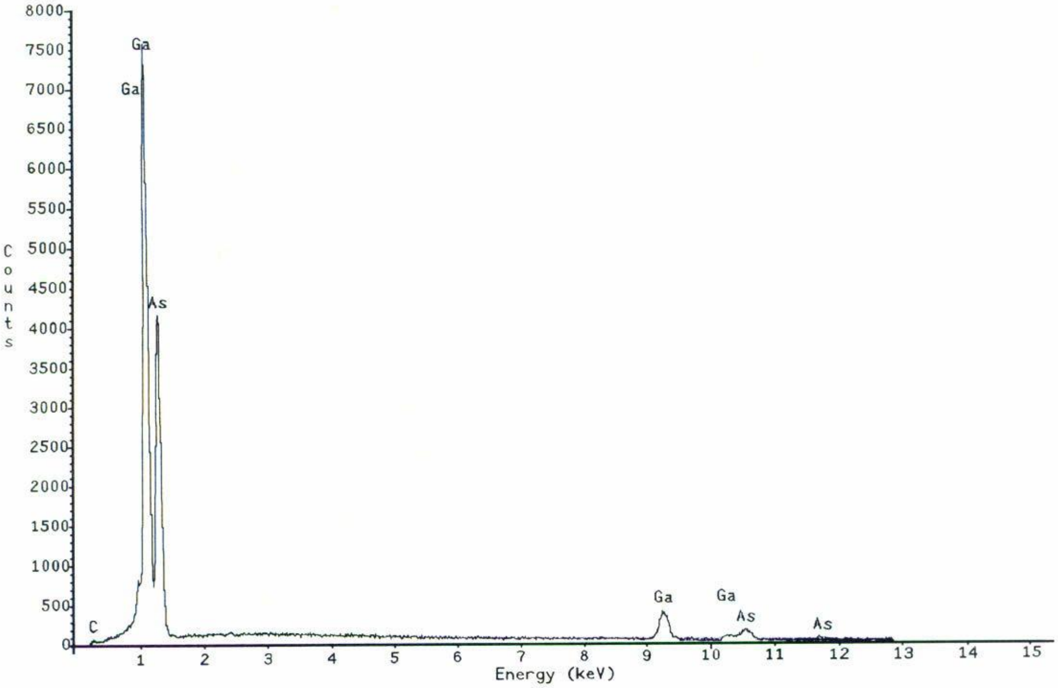


FIGURE 4. A representative EDS spectrum of the GaAs grown layers under study.

According to Pizzarello [14], a highly stepped surface occurs specially if the epitaxial growth is carried out on crystallographic planes not oriented in the (111) direction due to wide angular displacements tending to grow in the (111) direction. In one hand, this could be a partial cause for obtaining films with SK growth mode since (100) GaAs:Cr substrates have been used. In the other hand, the 4 SEM micrographs of Fig. 3, show clearly the effect of varying the spacer thickness, certainly one conclusion is that low GR such as the one produced by a spacer with thickness $\delta = 2$ mm results in a polycrystalline morphology, this image is 2000x magnified for its better visualization, see Fig. 4d.

4.2. EDS ANALYSIS

An EDS analysis was performed on different representative regions of each sample under study. According to this analysis the layers are rich in Ga [15] (in the average 52.28 atomic percent of Ga and 47.72 of As). The spectra of all samples also show a very weak signal corresponding to the residual contaminant C. This signal is slightly larger in layers with polycrystaline surface morphology. Fig. 4 shows a representative EDS spectrum of these GaAs layers. It is worthwhile to mention, that in our previous work [10] the GaAs layers besides C also presented Si and O contamination, thus, from the point of view of residual impurities, this means that the quality of GaAs layers has been improved.

The nonstoichiometry of the GaAs overlayers is due to the nature of the CSVT growth process. It is known, that the GaAs dissociates with preferential evaporation of arsenic at high temperature, and that the species leaving GaAs at evaporation are Ga and As_2.

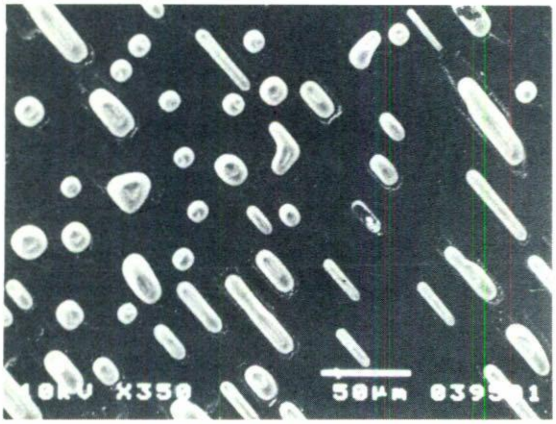


FIGURE 5. A SEM micrograph of the GaAs source showing the Ga droplets.

Under free evaporation, the temperature of congruence at which the composition of vapor phase is the same as in the solid phase is 657°C for the 100 face of GaAs [16]. Above this temperature the arsenic evaporation is dominant and the excess of Ga left coalesces into droplets.

Also Proix *et al.* [17] by the low energy electron diffraction technique, LEED, studied the surface phenomena of GaAs (110) through an annealing temperature range. One of their observations was, that beyond around 800°C, the topology of the surface changed to a (111) Ga face of GaAs with a 2×2 superstructure. Cho [18, 19] demonstrated not only that 2 or more structures exist for both (100) and $(\bar{1}\,\bar{1}\,\bar{1})$ GaAs but also that conversion between the structures is a function of crystal temperature and the relative fluxes of Ga and As_2 incident upon the surface in case of a MBE growth. He named the structures observed at lower crystal temperature and/or relative high As/Ga incident flux ratio as As-stabilized while the structures after high temperature treatment in vacuum with relative low As/Ga incident flux ratio as Ga-stabilized. In the other side, Kobayashi [20] proved that the atomic hydrogen reacts with the surface Ga atoms and removes them from the GaAs surface in the form of gallium hydride, GaH_3.

Due to the facts stated above, we think that during the growth process of GaAs with the CSVT system and atomic hydrogen as the only reactant, both effects of high temperature- and atomic hydrogen-etch take part.

Since the source-spacer-substrate is not a sealed assembly, the atomic hydrogen reacts with both faces of the GaAs source, forming volatile compounds as GaH_3. The Ga droplets due to the effect of high temperature dominant arsenic evaporation are observed in both sides of the GaAs source and shown in the SEM micrograph Fig. 5. It is very likely that the atomic hydrogen reacts with the As_2, forming AsH_3, which is also a volatile compound. Then, due to the existing thermal gradient between the source and the substrate, the volatile compounds migrate to the substrate, where they react inversely. At the moment, this last reaction is not well understood, but what is very probable is that the volatile species find not a stoichiometric (100) GaAs substrate surface but a Ga-stabilized surface structure or what is equivalent a (111)A plane due to the effect of

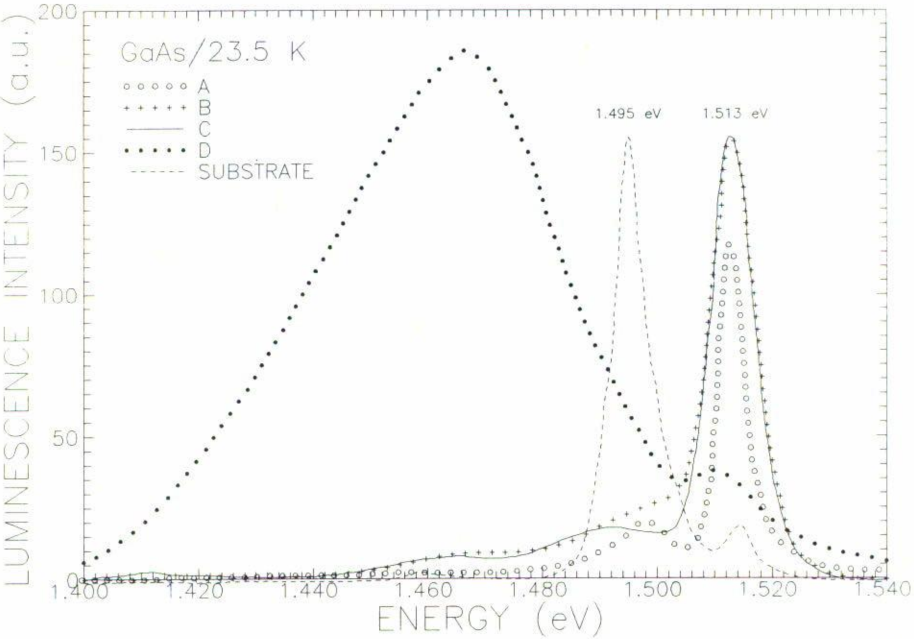


FIGURE 6. PL spectra at 23.5 K of the GaAs layers grown with a CSVT system and atomic hydrogen as the transport agent. A) corresponds to a layer grown with spacer thickness $\delta = 0.025$ B) $\delta = 0.6$, C) $\delta = 1$, and D) with $\delta = 2$ mm. The dashed line PL spectrum corresponds to the (100) GaAs:Cr substrate.

the substrate temperature, (stoichiometric in this instance, means that the number of Ga atoms on Ga lattice sites is equal to the number of arsenic atoms on As lattice sites). Probably a similar high temperature effect is the reason why Pizzarello [14] in his study of the nature of growth of GaAs on substrates of various crystallographic orientations observed a tendency of growth in the (111) direction. Up to this point, a logic question is: Does it really a GaAs layer grows? Or the surface morphologies shown in Fig. 3 are only the effect of high temperature substrate etch. Two facts answer this question: The weight difference before and after the growth process, indicates a gain in weight for the substrate but a more convincing proof is given by the PL measurements, see below.

4.3. PHOTOLUMINESCENCE STUDIES

Photoluminescence studies have been performed to obtain more information about the nature of the residual impurities of the layers under study. In these measurements it was used for excitation the 488 nm line of an Ar laser with 8 W/cm^2 power density incident on the sample at a temperature of 23.5 K. The Fig. 6 shows the PL spectra corresponding to the grown GaAs layers, whose surface morphologies are shown in Fig. 3. The spectra A, B, and C of Fig. 6 are dominated by a strong line at 1.513 eV, this line corresponds practically to the position of the free exciton at the temperature of 23.5 K (4 meV below E_g =1.517 eV for GaAs [21]). It is observed from these spectra that the half width of this line varies slightly for each surface morphology: ($\Delta h\nu = 10$ meV) for samples grown with $\delta = 0.6$ and 1 mm, whose morphologies are shown in Figs. 3b and 3c, and ($\Delta h\nu = 6$ meV) for the layer grown with $\delta = 0.025$ mm, whose surface morphology is shown in Fig. 3a. These half widths (6–10 meV) are too wide compared with the free exciton characteristic width ($\Delta h\nu = 1$ meV), we infer, that this band must be the superposition of some other lines, since in this region are found some excitonic transitions involving impurity levels such as the identified as (D°, X), (A°, X), (D°, h), and (D^+, X). The lack of structure in these lines is mainly due to an impurity concentration high enough to avoid resolving them [22]. Other lines in the PL spectra are the band at 1.493 eV, for which the carbon atoms occupying the As-vacancies are responsible [23], and the band at 1.46 eV, which is an LO phonon replica of the 1.493 zero phonon peak [23]. The PL spectrum of the substrate is included for comparison, see Fig. 6, its spectrum shows a very strong 1.493 band and a very weak band at 1.513 eV. This is a remarkable result, it indicates that, although the substrate is highly doped with carbon, the first 3 grown GaAs layers, present better quality. The carbon is an unintentional shallow acceptor, ubiquitous companion of the GaAs and other III-V compounds grown with many systems including the molecular beam epitaxy (MBE), whose source remains unclear [24], and it is not removable by heating. In the other side, PL spectra scanned along the radius of the samples are very similar, they present lines at the same energy positions with similar intensities under the same PL measurement conditions, this means that the GaAs overlayers are uniform in their elemental composition. Thus, observing the PL spectra A, B, C, we could conclude, that the GaAs overlayer grown with $\delta = 0.025$ mm, whose surface morphology is shown in Fig. 3a, is of better quality, since its 1.513 eV line presents smaller half width and its carbon line is weaker. Finally, the spectrum D is typical of a polycrystalline sample, which is in accord with the surface morphology, Fig. 3d. Partial results are submitted for examination however, further studies have to be made to answer satisfactorily the questions stated in the introduction section.

CONCLUSIONS

It was observed a phenomenological relationship among the spacer thickness, the growth rate parameter and the surface morphology of the grown GaAs layers: smaller spacer thickness produced higher growth rates and films with SK growth mode, the largest spacer thickness (2 mm) produced the lowest growth rate and a polycrystalline morphology. By EDS analysis we conclude that the GaAs overlayers have Ga-stabilized structure, we infer that the nonstoichiometry of these layers is due to the nature of the CSVT growth process and the atomic hydrogen as the reactant, in which the effects of high temperature and the interaction of the atomic hydrogen with the source and the substrate take part. Photoluminescence data show that all GaAs films except for the one with polycrystalline morphology, had a dominant near-gap emission at 23.5 K. It appears as a broad peak (6-10 meV) at 1.513 eV (4 meV below the band-gap emission). The near gap emission from the film grown with the smallest spacer thickness (0.025 mm) is more efficient, see open circles spectrum. The half width of this line is 6 meV. The 1.493 eV line is atributed to an emission originated from carbon atoms occupying the As-vacancies.

REFERENCES

1. F.H. Nicoll, *J. Electrochem. Soc.* **110** (1963) 1165.
2. P. Robinson, *RCA Rev.* **21** (1963) 574.
3. G.E. Gottlieb and J.F. Corboy, *RCA Rev.*, (1963) 585.
4. E. Sirtl, *J. Phys. Chem. Solids* **24** (1963) 1285.
5. N. Guelton, R.G. Saint-Jacques, D. Cossement, G. Lalande, and J.P. Dodelet, in *Microscopy of Semiconducting Materials*, edited by A.G. Cullis and N.J. Lang (Institute of Physics, Bristol, 1991), p. 415.
6. J. Mimila Arroyo, R. Castanedo, F. Chávez, R. González, G. Navarro, and A. Reynoso, *Appl. Phys. Lett.* **51** (1987) 2004.
7. E. Koskiade, D. Cossement, R. Paynter, J.P. Dodelet, A. Jean, and B.A. Lombos, *Can. J. Phys.* **67** (1989) 251.
8. Le Bel, D. Cossement, and J.P. Dodelet *J. Appl. Phys.* **73** (1993) 1288.
9. F. Silva-Andrade, F. Chávez, and E. Gómez, *J. Appl. Phys.* **76** (1994) 1946.
10. E. Gómez, R. Silva, and F. Silva-Andrade, *Rev. Mex. Fís.* **43**, 2 (1997) 290
11. N. Toyoda, M. Mihara, and T. Hara, *J. Appl. Phys.* **51** (1980) 392.
12. D. Côté, J.P. Dodelet, B.A. Lombos, and J.I. Dickson, *J. Electrochem. Soc.* **133** (1986) 1925.
13. H. Lűth, *Surfaces and Interfaces of Solids*, second edition (Springer Verlag, 1993).
14. Frank A. Pizzarello, *J. of Electrochem. Soc.* **110** (1963) 1059.
15. J.C. Brice, *Properties of Gallium Arsenide*, (EMIS Data Reviews series, No. 2, 1990), Chap. 2.
16. C.T. Foxon, J.A. Harvey, and B.A. Joyce, *J. Phys. Chem. Solids* **34** (1973) 1693.
17. F. Proix, A. Akremi, and Z.T. Zhang, *J. Phys. C: Solid State Phys.* **16** (1983) 5449.
18. A.Y. Cho, *J. Appl. Phys.* **41** (1970) 2780.
19. A.Y. Cho, *J. Vacuum Sci. Technol.* **8** (1971) S31.
20. R. Kobayashi, K. Fujii, and F. Hasegawa, in *Gallium Arsenide and Related Compounds*, edited by G.B. Stringfellow (Institute of Physics, Bristol, 1991), Chap. 2, p. 43.
21. S.M. Sze, *Physics of Semiconductor Devices*, second edition (John Wiley and Sons, New York, 1981), Chap. 1.
22. E.O. Kane, *J. Phys. Chem. Solids* **1** (1957) 249.
23. W.H. Koschel, S.G. Bishop, B.D. McCombe, W.Y. Lum, and H.H. Wieder, *Gallium Arsenide and related compounds*, second edition (Edinburg, 1976), p. 98.
24. Colin E.C. Wood, *The Technology and Physics of Molecular Beam Epitaxy*, edited by E.H.C. Parker (1985), Chap. 4.