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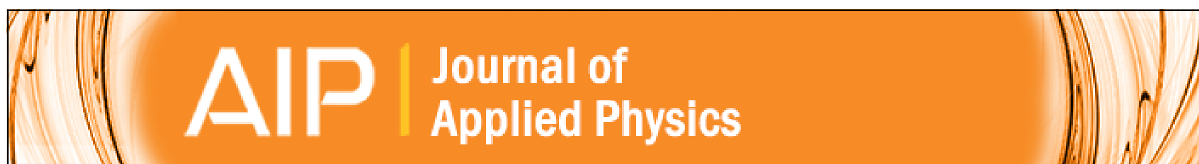

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Photoluminescence of GaAs films grown by vacuum chemical epitaxy

A. A. Bernussi, C. L. Barreto,[a] M. M. G. Carvalho, and P. Motisuke
DFESCM, IFGW, UNICAMP, 13081-Campinas-S.P., Brasil

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GaAs layers grown by vacuum chemical epitaxy (VCE) are investigated by low-temperature photoluminescence. A qualitative relation between the growth parameters and the shallow-impurity-incorporation mechanism is established. It was observed that the predominant shallow acceptor is carbon, and its incorporation during the growth process decreases with the As:Ga ratio, increases with growth temperature until 750 °C, and then it diminishes. In this work we compare the characteristics observed in the VCE system with those in conventional molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD). Our results show that this system contains some advantages from both the MBE and MOCVD systems. The photoluminescence spectra also show that at low As:Ga ratios the generation of As vacancies or its complexes is strongly enhanced.

I. INTRODUCTION

Vacuum chemical epitaxy (VCE) is a process in which epitaxial layers are grown by reacting the group-III alkyl molecules and the group-V hydrides in a high-vacuum system.[1–4] The initial pressure in the chamber is pumped down to $(2–3)\times 10^{-8}$ Torr with a turbo-molecular pump, and the residual gases are monitored with a quadrupole mass analyzer. During the growth process the total pressure in the chamber is approximately 10^{-3} Torr. As pointed out by Fraas *et al.*,[4] the VCE system combines the technology of the conventional metalorganic chemical vapor deposition (MOCVD) and the high-vacuum, safety, and excellent material control of the molecular-beam epitaxy (MBE) systems. As a result, the following characteristics of the VCE system can be outlined: (i) no carrier gas is needed to introduce the reagent molecules into the chamber; (ii) the utilization efficiency of the reactant molecules is very high; (iii) the gaseous-phase reactions take place in a vacuum environment; (iv) the molecular flow from the gas source is easier to control than a molecular beam from solid or liquid sources; (v) the relatively low cost of the system and the high utilization efficiency of the expensive reactant gases contribute to make the III-V compound device a medium-cost product. Until now, there is no detailed study, using low-temperature photoluminescence (PL), of the III-V compound layers grown by VCE. Therefore, the aims of this present work are to study the PL the influence of the growth parameters on the quality of the GaAs layers and to compare these results with those published for MOCVD and MBE systems. All GaAs films studied in this work were grown on Cr-doped or undoped semi-insulating GaAs substrates, using a 1:1 arsine-hydrogen mixture and pure triethyl-gallium (TEGa) as growth precursors. This resulted in semi-insulating or highly resistive *p*-type layers with good morphologies and mirrorlike surfaces. As shown in Table I, growth rates varying from 0.25 to 0.80 μm/h are strongly dependent on the As:Ga flow ratio and to a lesser extent on the growth temperature (T_g). In these conditions the growth rate is lower than that in the conventional MOCVD system operating at low[5] or atmospheric pressure.[6] The electrical characterization made in some samples consisted of standard van der Pauw Hall measurements at 300 K, and the results obtained for mobility and carrier concentration are of the order of 300 cm^2/V s and 5×10^{15} cm^{-3}, respectively. The AsH_3:TEGa ratio (or V:III ratio) was varied from 8 to 24 by changing the AsH_3 flow rate, and T_g was varied from 650 to 850 °C.

[a] Present address: Depto. de Fisica/UFRN, C.P.:1524-Natal-59072-RN-Brasil.

II. OPTICAL CHARACTERIZATION

A. Photoluminescence experiments

The low-temperature photoluminescence measurements were carried out with samples immersed in liquid helium pumped down to 2 K and excited with the 514.5-nm line of an Ar^+ laser or with the 632.8-nm line of a He-Ne laser. The power density employed was 2 mW/cm^2 at the lower limit and 2 W/cm^2 at the highest excitation. The luminescence radiation was analyzed with a 0.5-m grating spectrometer, with spectral resolution better than 0.2 meV, and detected with a liquid-nitrogen-cooled S1 photomultiplier. The PL spectra measurements at increasing temperatures were performed with the samples placed in a cold-finger-type cryostat under low excitation conditions.

B. Experimental results and discussion

Figure 1 shows a typical photoluminescence spectrum at 2 K for a GaAs layer grown by VCE with $T_g = 750$ °C and As:Ga = 24. We can distinguish two main regions[7–9]: The

TABLE I. Growth parameters of GaAs films obtained in the VCE system.

Sample No.	T_g (°C)	As:Ga	Growth rate (μm/h)
45	650	24	0.37
47	700	24	0.37
54	750	24	0.15
49	800	24	0.25
40	750	16	0.48
52	750	12	0.62
56	750	8	0.80

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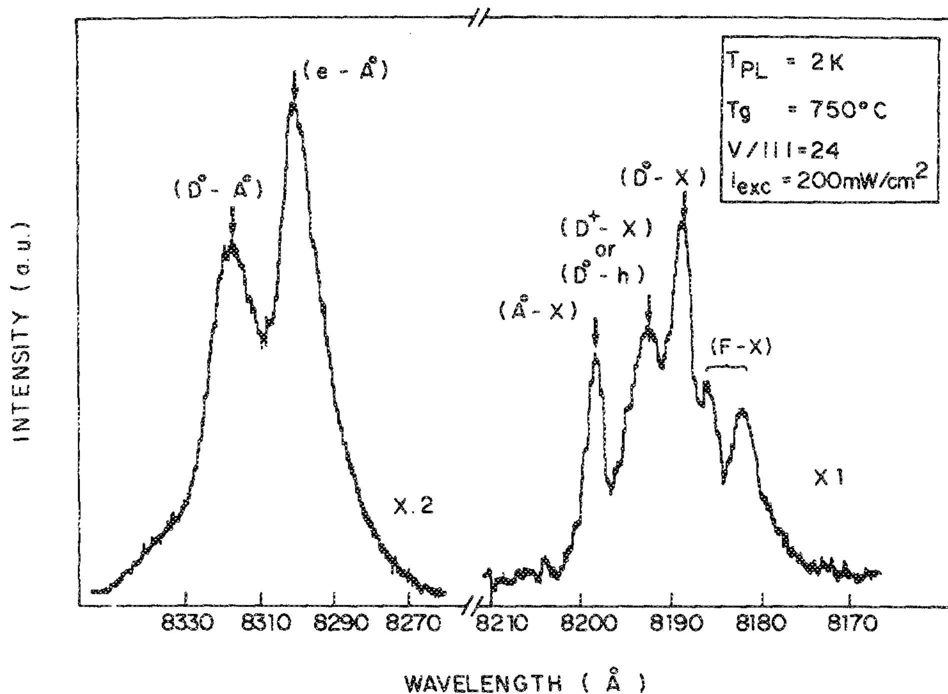

FIG. 1. Typical photoluminescence spectrum at 2 K of a GaAs film grown at T_g = 750 °C and As:Ga = 24, in the VCE system.

first region, from 8176 to 8214 Å (or 1.516–1.509 eV), is due to the camel-back structure commonly observed in free-exciton emission[10,11] (F-X), bound-exciton to neutral-donor (D^0-X), bound-exciton to ionized-donor (D^+-X) [or valence-band to neutral-donor transition (D^0-h)], and bound-exciton to neutral-acceptor (A^0-X) transitions.[12] The second region, from 8300 to 8460 Å (or 1.494–1.465 eV), is due to conduction-band–acceptor (e-A^0) and donor-acceptor (D^0-A^0) transitions.[7] The identification of these acceptor impurity bands was done from the analysis of the spectra taken by varying the excitation intensity (I_{exc}) and sample temperature (T_{PL}) as shown in Fig. 2. With increasing I_{exc} the (D^0-A^0) peak [Fig. 2(a)] transition shifts[13] to higher energies while the e-A^0 transition practically does not shift at all. The latter transition dominates[14] the spectra at high I_{exc} values due to saturation of the D^0-A^0 recombination. With increasing T_{PL} [Fig. 2(b)], the electrons in the shallow donor levels are thermally ionized to the conduction band and the relative intensity of the D^0-A^0 line strongly decreases. Thus e-A^0 transition dominates the spectrum at T_{PL} values greater than 15 K. This spectral behavior leads us to ascribe the emission at 1.4909 eV to D^0-A^0 recombination and the 1.4935-eV emission to the e-A^0 transition. The acceptor ionization energy (E_A) was calculated from the luminescence maximum of the e-A^0 band using Eagles' rule[15] as $E_A = 26.5$ meV, a value closely related to C_{As}.[7]

Figure 3 illustrates the PL spectra in the excitonic and donor-acceptor regions for GaAs films grown at ratio As:Ga = 24 but with different T_g values. From these spectra one can clearly see the effect of the growth temperature on the quality of these layers, with respect to the PL line separation, that it is better for intermediate temperatures ($700 < T_g < 750$ °C) and very poor at extreme temperatures. To study the carbon-incorporation mechanism in these epilayers, we plot in Fig. 4 the normalized intensity of the e-C_{As} transition band (normalized to the total integrated intensity of each spectrum) versus the reciprocal of T_g.[16] The e-C_{As} transition intensity increases up to 750 °C and beyond this temperature it decreases. This is distinctive behavior when it is compared with the monotonic increase with T_g, observed in GaAs samples grown by MOCVD systems.[17] The main source of carbon impurities is probably TEGa,[17,18] but we did not discard the possibility of other sources of carbon contaminants such as the reactor walls and the graphite heater. The TEGa thermal decomposition is almost complete[19–21] at the usual growth temperature used in the VCE system. Since the pressures employed are low, the surface

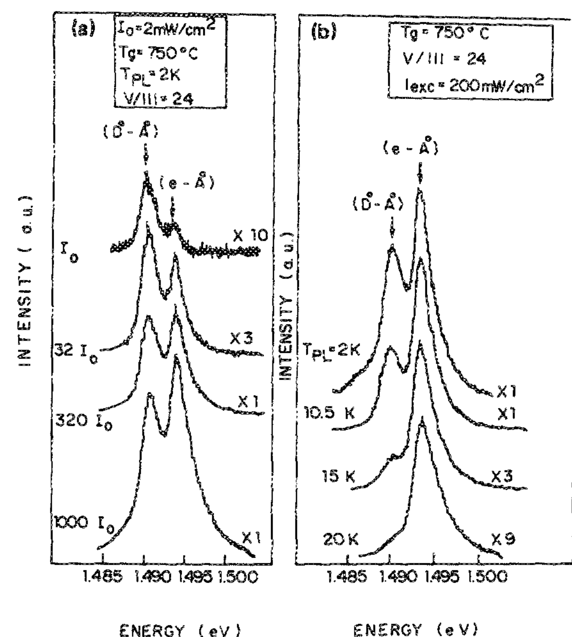

FIG. 2. Conduction-band–acceptor (e-A^0) and donor-acceptor (D^0-A^0) recombination dependence on (a) intensity excitation and (b) photoluminescence temperature.

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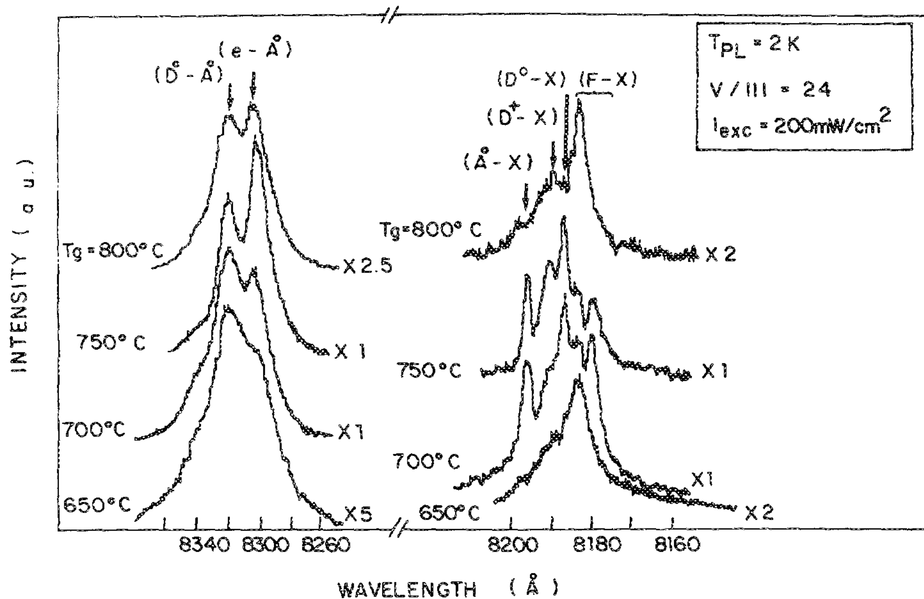

FIG. 3. Photoluminescence spectra at 2 K of GaAs layers grown at As:Ga = 24 and with different T_g values.

reactions will be more important than the gaseous-phase reactions and the GaAs substrate will act as a catalyzer. When the TEGa molecules hit the surface, the ethyl radicals are transferred to the growing surface and many carbon atoms could be adsorbed in the layer. The reaction path for this impurity-incorporation mechanism is not well established yet, but the observations made by Fraas *et al.*[4] indicate the presence of ethane (C_2H_6) that is probably generated by hydrogenation of the ethyl radical. They also observed the presence of ethylene (C_2H_4) as a residual gas, probably coming from spontaneous decomposition of the ethyl radicals, leaving a hydrogen atom behind on the surface. The arsine thermal decomposition efficiency changes drastically in the temperature range 650–710 °C,[22] giving rise to a large quantity of As_2 species and hydrogen atoms at high T_g values. This increases the arsenic pressure near the growing layer, reducing the formation of the arsenic vacancy.[23] Another important feature that one has to take into consideration is the effect of substrate heating. When the substrate is heated from 550 to 750 °C, the As_2 and the Ga vapor pressures, due to arsenic and gallium evaporation from the substrate, increase by 5 and 4 orders of magnitude,[24] respectively, and at high T_g values, the As_2 vapor pressure is greater than the Ga partial pressure. The last point that is also relevant is the gallium incorporation rate as a function of the growth temperature. Takahashi *et al.*[25] reveal that in the atmospheric-pressure MOCVD using trimethyl-gallium and arsine sources, the Ga incorporation rate decreases monotonically with T_g. Chang, Chen, and Nee[26] observed in the low-pressure MOCVD using triethyl-gallium and arsine sources a monotonic increase of the Ga incorporation rate with T_g. These works both clearly show that the Ga incorporation rate strongly depends on the particular system and the Ga-source material.

From the above discussion we could tentatively explain the observed carbon-incorporation mechanism in GaAs films grown by VCE as follows: (i) The increase in the carbon incorporation up to 750 °C is probably related to a lower efficiency of the arsine thermal decomposition. This results in a low-vapor pressure of As_2 and atomic hydrogen. The former is not sufficient to counterbalance the As_2 evaporation from the growing surface, and the latter is not enough to eliminate the hydrocarbon radicals at the growing surface by hydrogenation. Consequently, more carbon impurities are favored to enter As sites, increasing the acceptor incorporation (ii) Above 750 °C (see Fig. 4) less carbon incorporation is observed, suggesting that the arsine thermal decomposi-

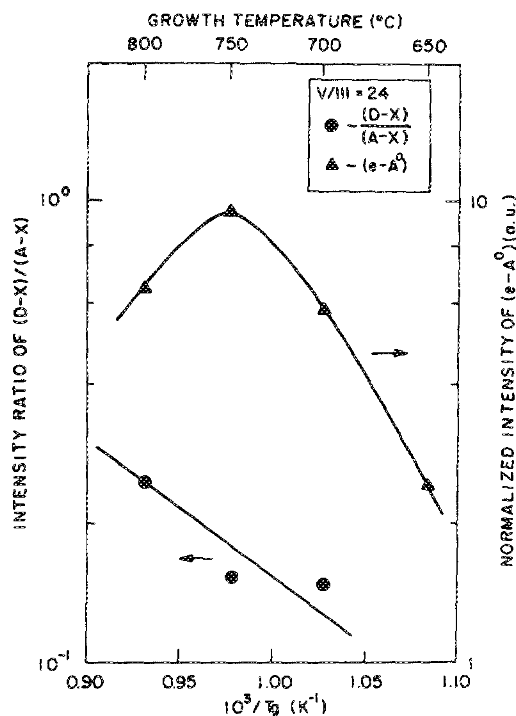

FIG. 4. Ratio of the peak intensity of $I(D\text{-}X)/I(A\text{-}X)$ transitions (left ordinate) and the normalized intensity of $e\text{-}A°$ transition (right ordinate) as a function of the reciprocal growth temperature.

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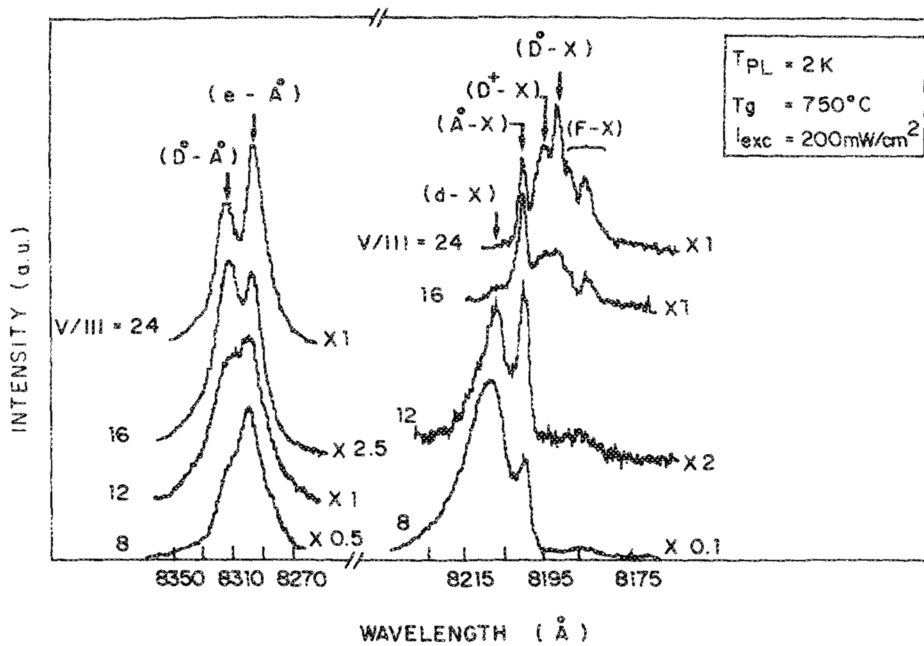

FIG. 5. Photoluminescence spectra at 2 K of GaAs layers grown at $T_g = 750\,^{\circ}\mathrm{C}$ and with different As:Ga ratios.

tion becomes more efficient and more As_2 species and hydrogen atoms are generated. To give a qualitative idea of the residual donor incorporation ratio, we also plot in Fig. 4 the relation between the sum of the peak intensities of the emission lines related to the bound-exciton to donor transition $[(D^0\text{-}X) + (D^+\text{-}X)]$, which we call $D\text{-}X$, and the line related to the bound-exciton to acceptor transition $(A\text{-}X)$,[16] as a function of the reciprocal of T_g. The increase in the intensity ratio $I(D\text{-}X)/I(A\text{-}X)$ with increasing T_g, suggests that the donor incorporation rate is greater than the acceptor incorporation rate.

Figure 5 shows the PL spectra of GaAs layers grown at $T_g = 750\,^{\circ}\mathrm{C}$ and different As:Ga ratios. From these spectra we observe a strong dependence of the emission line separation with the flow ratio. The line separation increases as the As:Ga ratio increases, indicating that high-quality GaAs films can be obtained in the VCE system, for higher values of the As:Ga ratio. To illustrate the carbon incorporation in these epilayers, we plotted in Fig. 6 the normalized intensity of the $e\text{-}C_{As}$ transition as a function of the As:Ga ratio. The intensity of this line increases with decreasing As:Ga flow, suggesting[17] that at low As:Ga ratios more As vacancies are generated, and consequently more carbon impurities are favored to enter into As sites, increasing the carbon incorporation. It is also shown in Fig. 6 the peak intensity ratio $I(D\text{-}X)$

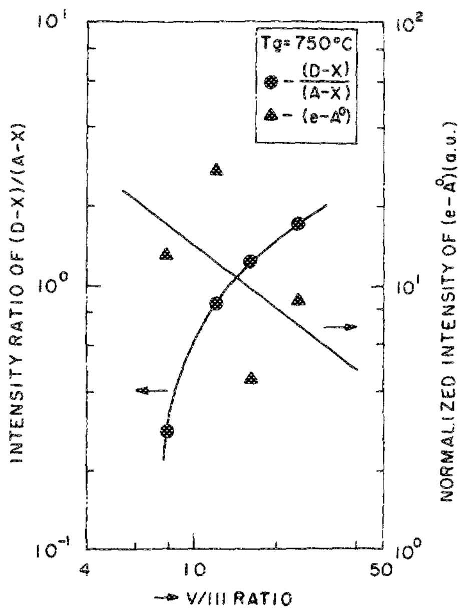

FIG. 6. Ratio of the peak intensity of $I(D\text{-}X)/I(A\text{-}X)$ (left ordinate) and the normalized intensity of $e\text{-}A^0$ (right ordinate) as a function of the As:Ga flux.

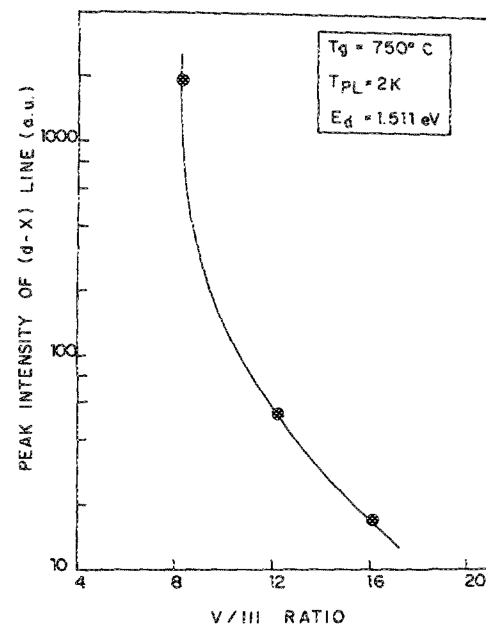

FIG. 7. Defect–bound-exciton $d\text{-}X$ (at $E_d = 1.511$ eV) peak intensity as a function of the As:Ga flow.

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$/I(A\text{-}X)$ as a function of the As:Ga ratio. The donor's average incorporation rate at low As:Ga ratios is higher than the acceptor's incorporation rate, and at high As:Ga values this incorporation rate tends to be reversed.

In the spectra of Fig. 5, we observe a strong emission line at $E_d = 1.511$ eV, which was attributed[27,28] to a "defect-induced" bound exciton (d-X), and it strongly depends on the As:Ga ratio. The peak intensity of this band as a function of the As:Ga ratio is plotted in Fig. 7, from where we can observe a drastic enhancement of this line intensity when the As:Ga flow ratio is reduced. In contrast to GaAs samples grown by MBE,[29] high T_g values do not eliminate the d-X line intensity. From Fig. 5 we can also observe that the peak intensities of the A^0-X and d-X lines decrease with increasing As:Ga ratio. This is an indication that these defects may be related to complexes involving the carbon acceptor impurity and an arsenic vacancy, which we believe to be present at high concentrations in samples grown at low As:Ga values. However, we did not observe any line related to the "defect complex," as generally observed in GaAs samples grown by MBE.[29]

III. CONCLUSIONS

The undoped GaAs layers grown in the VCE system over the range of $650 \leqslant T_g \leqslant 800$ °C and $8 \leqslant$ As:Ga $\leqslant 24$, using as source material TEGa and arsine, are all semi-insulating or high-resistivity p-type material; their growth rate is lower than that observed in the conventional MOCVD system. The photoluminescence characterization of these GaAs layers showed that the predominant residual shallow acceptor impurity is carbon. The defect-associated exciton line at 1.511 eV is strongly enhanced at low As:Ga ratio. An empirical relation between residual shallow impurities (C_{As}, donors, and defects) and the growth parameters (T_g and As:Ga ratio) was obtained. In some extent these relations are characteristics of the VCE system, and under the point of view of the photoluminescence efficiency and its spectral resolution, good GaAs layers can be grown in the VCE system with $T_g \sim 750$ °C and As:Ga ~ 24. However, when compared with GaAs samples grown by liquid-phase epitaxy (LPE), the VCE ones exhibit low PL efficiency, suggesting a quite high incorporation rate of deep-level impurities. The incorporation mechanism of the latter will be the subject of a forthcoming study.

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