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Residual impurities in MO-VPE GaAs epitaxial layers

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Résumé. — La nature et la concentration des impuretés résiduelles dans des couches de GaAs élaborées par épitaxie en phase vapeur à partir de composés organométalliques ont été analysées en fonction des paramètres de croissance : température, rapport As/Ga dans la phase vapeur, excès de CH_4 . Les spectres de photoluminescence (PL) montrent que l'impureté résiduelle la plus importante est le carbone. La concentration de carbone résiduel augmente avec la pression de CH_4 . Un pic de PL apparaît à 1,477 eV dans les échantillons recuits sous atmosphère de AsH_3 . Les propriétés de ce pic sont interprétées par l'apparition d'un accepteur d'énergie d'activation = 40 meV, différent du germanium.

Abstract. — The nature and concentration of residual impurities in MO-VPE GaAs layers were studied as a function of growth parameters : temperature, ratio As/Ga, excess CH_4 in the gas phase. Photoluminescence (PL) spectra show that the main residual impurity is C. The amount of residual C increases with excess CH_4 . A PL peak at 1.477 eV appears for samples annealed under AsH_3 . The properties of this peak are interpreted in terms of a 40 meV deep acceptor, not related to germanium.

Introduction.

Gallium arsenide devices are currently of considerable interest for a wide variety of applications. These devices were usually grown by LPE, halide VPE ($\text{Ga-AsCl}_3\text{-H}_2$), MBE and MO-VPE.

LPE has demonstrated high quality GaAs $\mu_{77} \gtrsim 300\,000\text{ cm}^2/\text{V.s}$ [1], halide VPE has reached $\mu_{77} = 200\,000\text{ cm}^2/\text{V.s}$ [2]. MO-VPE and MBE have not reached yet these standards (the best value reported for μ was about $150\,000\text{ cm}^2/\text{V.s}$) for both methods [3, 4]. However high performance devices have been manufactured using MO-VPE including FET, DH-lasers, quantum well hetero-structures and solar cells.

Since the pioneer work of Manasevit [5], MO-VPE is widely used for laboratory scale production of devices. Basically GaAs deposition occurs through irreversible pyrolysis of trimethylgallium (TMG) and AsH_3 on only one hot zone. Due to the absence of

halides no corrosion of the pipes occurs neither does reaction with quartz walls. Auto-doping is thus eliminated.

Residual impurities in non intentionally doped GaAs result mainly from impurities in the starting TMG and AsH_3 . High quality-electronic grade-sources are needed to obtain low residual impurities concentration together with efficiently leak tested MO-VPE apparatus.

Native defects in GaAs (V_{Ga} , V_{As} , As_i , As_{Ga}) together with complexes (D-V_{Ga} ...) are well known [6] and their concentration depends on the growth process. Incorporation of residual impurities from TMG and AsH_3 is strongly dependent on the experimental conditions : deposition temperature T_D , ratio As/Ga in the gas phase, pressure.

Three kinds of impurities are incorporated in the epilayers : i) shallow donors or acceptors which come from the starting chemicals (TMG or AsH_3), like Si, Zn or Mg; ii) impurities which come from the decomposition products of TMG, and iii) O which cannot be completely eliminated from H_2 . The goal of the present paper is to identify the residual impu-

(*) This work is part of the thesis presented by B. El Jani to get the « Docteur 3^e cycle » degree, May 1982, Paris VII.

rities, mostly carbon, and to correlate their densities with experimental conditions. Excess CH_4 was purposely introduced to enhance the carbon contamination.

1. Experimental.

Experiments were carried out in a conventional horizontal reactor (Fig. 1). All the tubing was carefully leak tested. Hydrogen is purified on a Pd cell. Residual O_2 and H_2O can be measured using an O_2 and H_2O detector respectively.

TMG was supplied by Labolac or Alfa; AsH_3 10 % in 99.999 9 % H_2 was obtained from Air Liquide or Matheson.

[100] semi insulating Cr-doped GaAs substrates were obtained from MCP, MR or RTC (France). They are mechanochemically polished by the manufacturers. Before being used they are cleaned in hot trichlorethylene, acetone, then etched for 20 s in (5 : 1 : 1) mixture (H_2SO_4 : H_2O_2 : H_2O) finally rinsed in D.I water and blown dry with filtered argon before being loaded into the reactor.

Experiments were carried out between 630 and 730 °C. The ratio As/Ga varied between 2 and 100. The total flow of H_2 was 1 800 ml/min. The partial pressure of TMG was 10^{-4} atm.

Some experiments were carried out in a partial pressure of CH_4 .

1.1 CHARACTERIZATION. — The electrical properties (ρ , carrier density, ...) were measured using standard Van der Pauw's method and the layer thickness was measured by optical microscopy. The standard thickness used was 6 μm ⁽¹⁾. The compensation ratio was deduced from low temperature measurements [8-10].

Low temperature photoluminescence measurements were performed at 1.6 or 4.2 K. The PL was excited with a dye laser (2 mW) with typical photon energy of 2 eV.

The spectrometer used was a grating monochromator with 1.10 meter focal length. The detector was a cooled GaAs photomultiplier (RCA 1304) with either photons counting or lock in amplifying techniques. The laser was focused on about a 100 μm diameter spot.

2. Experimental results.

2.1 GENERAL FEATURES. — As most of authors involved in MO-VPE of GaAs did [5, 7, 11, 12], we verified that the growth rate is independent of the temperature of the substrate in the range 630-730 °C (Fig. 3), and it is linearly dependent on the partial pressure of TMG (Fig. 4). A completely consistent

⁽¹⁾ It has been established that the mobility increases with thickness to reach its maximum value at about 20 μm [7] : in this study, MO-VPE was done at atmospheric pressure, and the thickness of samples was usually chosen to be 6 μm or less to keep a specular surface.

Fig. 1. — MO-VPE horizontal reactor : general scheme.

Fig. 2. — Growth rate as a function of the AsH_3 partial pressure.

Fig. 3. — Growth rate as a function of the temperature.

Fig. 4. — Growth rate as a function of the TMG partial pressure.

explanation of these features has not been presented so far.

2.2 RESIDUAL DOPING. — The control and knowledge of the residual doping is of critical importance for the design of GaAs devices. It was studied as a function of the ratio As/Ga in the vapour phase (all other parameters kept constant) and as a function of the temperature (As/Ga kept constant).

2.2.1 Influence of the As/Ga ratio. — Table I gives some significant electrical properties of GaAs epitaxial layer (~ 5 μm thick) as a function of growth parameters T_D, As/Ga.

The figure 5 shows N_D - N_A (or N_A - N_D) as a function of As/Ga. As already observed by several authors, N_D - N_A increases with As/Ga to reach a maximum value, then slightly decreases.

This can be explained as follows :
— AsH₃ and TMG contain a small amount of residual impurities
AsH₃ : SiH₄, H₂O, Zn
TMG : Zn, Mg

— Free radicals coming from the pyrolysis of TMG may react with the quartz reactor and give volatile Si compounds. The pyrolysis of TMG produces CH₄ and C may be incorporated.

— The density of residual defects like V_{As} or V_{Ga} strongly depends on the growth conditions, more precisely of T_D and the ratio As/Ga.

Impurities and residual defects are incorporated during the growth process. Following Mullin [13], the incorporation of GaAs into the GaAs surface by MO-VPE may be written :

— It is generally established that growth experiments were done under mass-transport limited conditions (boundary layer model). The incorporation of group VI donors impurities occurs as follows

with $n \propto P_{\text{AsH}_3}^{-1}$.
The incorporation of group II acceptors is given by

with $p \propto P_{\text{AsH}_3}$.

Table I. — Electrical properties (*) of GaAs epitaxial layers (< 5 μm) non intentionally doped.

Run	As/Ga	T °C	(μm . min. ⁻¹) growth rate (**)	ρ (300 K) Ω cm ⁻¹	μ (300 K) cm ² /V.s	μ (77 K) cm ² /V.s	N _D - N _A (77 K) cm ⁻³	K (***)	N _D ⁺	N _A ⁻
03-029	6	680	0.07	0.83	2 360	7 400	2.5 . 10 ¹⁵	0.86	1.8 . 10 ¹⁶	1.5 . 10 ¹⁶
03-009	7.5	—	0.07	0.18	4 300	12 500	5.6 . 10 ¹⁵	0.6	1.4 . 10 ¹⁶	8.4 . 10 ¹⁵
03-028	11	—	0.07	0.14	4 600	11 900	6.9 . 10 ¹⁵	0.57	1.6 . 10 ¹⁶	9.1 . 10 ¹⁵
03-031	15	—	0.07	0.16	4 400	14 700	5.9 . 10 ¹⁵	0.52	1.2 . 10 ¹⁶	6.4 . 10 ¹⁵
03-039	37	—	0.08	0.08	6 000	19 600	9 . 10 ¹⁵	0.24	1.2 . 10 ¹⁶	2.8 . 10 ¹⁵
02-048	15	630	0.08	0.08	5 100	16 000	1.5 . 10 ¹⁵	0.77	6.5 . 10 ¹⁵	5 . 10 ¹⁵
03-001	—	650	0.08	0.31	5 600	22 150	2.7 . 10 ¹⁵	0.53	5.8 . 10 ¹⁵	3.1 . 10 ¹⁵
03-031	—	680	0.08	0.16	4 400	14 700	5.9 . 10 ¹⁵	0.52	1.2 . 10 ¹⁶	6.4 . 10 ¹⁵
02-050	—	730	0.10	0.07	5 200	13 700	1.1 . 10 ¹⁶	0.39	1.8 . 10 ¹⁶	7 . 10 ¹⁵
CD-022 A	15	680	0.1	etched	6 900	23 500	7.5 . 10 ¹⁵	0.1	8.5 . 10 ¹⁵	10 ¹⁵

(*) Van der Pauw measurements.
(**) The growth rate was kept constant, i.e. P_{TMG}. The ratio As/Ga in the gas phase in changed by changing P_{AsH₃}.
(***) From W. Walukiewics, L. Lagowski and H. C. Gatos, *J. Appl. Phys.* 53 (1982) 769.

On the other hand, group IV impurities like Si or C have an amphoteric behaviour. They are incorporated in Ga site as donors :

and as acceptors in As sites

From (3), (4) and (1), (2) it is deduced :

$$\frac{|\text{V}_{\text{Ga}}|}{|\text{V}_{\text{As}}|} = \frac{K_2}{K} \frac{P_{\text{AsH}_3}}{P_{\text{TMG}}} \frac{(P_{\text{CH}_4})^3}{(P_{\text{H}_2})^3} \quad (5)$$

and

$$\frac{|\text{Si}_{\text{Ga}}|}{|\text{Si}_{\text{As}}|} = K \frac{|\text{V}_{\text{Ga}}|}{|\text{V}_{\text{As}}|} = K' \frac{P_{\text{AsH}_3}(P_{\text{CH}_4})^3}{P_{\text{TMG}}(P_{\text{H}_2})^3}. \quad (6)$$

The same relation is also valid for the ratio $|\text{C}_{\text{Ga}}/\text{C}_{\text{As}}|$.

According to equation 6, an increase of the ratio As/Ga enhances the incorporation of group IV element as donor. Furthermore the amphoteric behaviour of Si and C depends on the temperature. The ratio $|\text{Si}_{\text{Ga}}/\text{Si}_{\text{As}}|$ or $|\text{C}_{\text{Ga}}/\text{C}_{\text{As}}|$ is temperature dependent. This means that the compensation depends on the growth temperature ⁽²⁾.

Residual defects incorporation was analysed in detail by Samuelson [14]. It is well established that

Samuelson using earlier results from Hurle [6] shows the following dependence :

$$\begin{aligned} |\text{V}_{\text{As}}| &\propto P_{\text{AsH}_3}^{-1} \\ |\text{V}_{\text{As}}^+| &\propto (P_{\text{AsH}_3})^{-1/2} \\ |\text{V}_{\text{Ga}}| &\propto P_{\text{AsH}_3} \\ |\text{V}_{\text{Ga}}^-| &\propto (P_{\text{AsH}_3})^{1/2} \\ |\text{As}_i| &\propto P_{\text{AsH}_3} \\ |\text{As}_i^+| &\propto (P_{\text{AsH}_3})^{1/2}. \end{aligned}$$

High AsH_3 pressure enhances the formation of interstitial arsenic and gallium vacancies. Complexes with Si_{Ga} or Si_{As} or C_{As} may be formed. The density of these complexes is very sensitive to heat treatment under As atmosphere.

2.2.2 Influence of the deposition temperature. — The figure 6 and figure 7 respectively show the variation of $N_{\text{D}} - N_{\text{A}}$ and the 77 K mobility as a function of the deposition temperature T_{D} for two different As/Ga ratio. As discussed earlier the incorporation of residual defects or impurities is mainly controlled by the

Fig. 5. — $(N_{\text{D}} - N_{\text{A}})$ as a function of the ratio As/Ga in the gas phase : $T_{\text{D}} = 680^\circ\text{C}$ (same TMG and AsH_3 sources).

temperature and P_{AsH_3} . From the shape of the curves on figure 6, it appears that a donor impurity is increasingly incorporated as the temperature increases, with a saturation at about 700°C , because the net carriers concentration increases while the mobility decreases from 650°C .

The compensation ratio $K = N_{\text{A}}^-/N_{\text{D}}^+$ remains high (≈ 0.6) for low As/Ga ratio (≈ 15) or at temperatures lower than 680°C (table I). For As/Ga = 15 (sample 03-031) or higher deposition temperature ($\approx 700^\circ\text{C}$) (sample 02-050), donor impurities are preferentially incorporated, K becomes ≈ 0.5 ; the shape of the dependence of the mobility on T_{D} can be qualitatively explained by the competitive effect of the temperature on the residual donors density (increase) and on the compensation ratio (decrease).

It is assumed that Si is the main donor impurity (and C the main acceptor), although both Si and C present an amphoteric behaviour.

For MBE [19] or LPE [6] Si doped GaAs epilayer, the ratio $\text{Si}_{\text{Ga}}^+/\text{Si}_{\text{As}}^-$ was experimentally found to be :

$$\text{Log} \frac{\text{Si}_{\text{Ga}}^+}{\text{Si}_{\text{As}}^-} = \text{Log} \gamma + \frac{A}{T} \quad (7)$$

where γ is the ratio Ga/As in the liquid or in the vapour.

⁽²⁾ For low doping levels Si is mostly incorporated as a donor $\text{Si}_{\text{Ga}} \gg \text{Si}_{\text{As}}$ whereas C_{As} is the main acceptor [7]. But in MO-VPE GaAs samples, Si_{Ga} is believed to be the main donor.

Fig. 6. — $(N_D - N_A)$ as a function of the deposition temperature (a) As/Ga = 7.5, (b) As/Ga = 15.

On the contrary in MO-VPE the Si_{Ga}^+ incorporation increases with the temperature and it was found that $\text{Si}_{\text{Ga}} \propto T_D$ when SiH_4 was used as an n type dopant [13]. Dapkus *et al.* [7] reported that C incorporation increases with T_D . To get information on C incorporation as donor and acceptor, experiments were done with excess CH_4 .

It must be mentioned that C contamination can be avoided when starting from triethylgallium (instead of TMG) and arsine [20, 21]. The electronic qualities of GaAs prepared by this way are high, however the growth rate is very low.

2.2.3 Influence of excess CH_4 . — Although the growth of GaAs by MO-VPE is a non equilibrium process, the reaction [1] should be shifted towards the reverse direction by addition of extra CH_4 in the gas phase. According to equation 5 the incorporation of group IV donors (in Ga site) should be enhanced by CH_4 .

Experiments were carried out with excess CH_4 in the following conditions :

$$\begin{aligned} T_D &= 680^{\circ}\text{C} \\ \text{As/Ga} &= 15 \\ 10^{-4} &< P_{\text{CH}_4} < 10^{-2} \text{ atm.} \end{aligned}$$

Fig. 7. — 77 K mobility of GaAs layers as a function of the deposition temperature, (a) As/Ga = 7.5, (b) As/Ga = 15.

It was experimentally established that the speed of deposition

$$V \propto P_{\text{CH}_4}^{-0.25}$$

and the residual impurities

$$N_D - N_A \propto P_{\text{CH}_4}^{0.25}.$$

From a standard chemical equilibrium as described by (1) a $(P_{\text{CH}_4})^3$ dependence of $N_D - N_A$ should be expected. However add-compounds with general formula $\text{Ga}(\text{CH}_3)_{3-x}\text{-AsH}_{3-x}$ with $x < 2.2$ were assumed to be formed and the final GaAs layer is grown by successive elimination of CH_4 molecules [13].

The μ_{77} goes down from $21\,000 \text{ cm}^2/\text{V.s.}$, $n \simeq 10^{15} \text{ cm}^{-3}$, to $13\,000 \text{ cm}^2/\text{V.s.}$, $n = 2 \times 10^{16} \text{ cm}^{-3}$, for a partial pressure $P_{\text{CH}_4} = 10^{-2} \text{ atm.}$

Growth of GaAs layers with excess CH_4 gives highly compensated layers by incorporation of C donors and acceptors. The higher the temperature, the greater the residual doping of the layers.

Post growth annealing.

In Si doped GaAs $n \gtrsim 10^{18} \text{ cm}^{-3}$, annealing at moderate temperature results in redistribution of Si among donor and acceptor sites and the formation of $\text{Si}_{\text{As}}^-\text{-Si}_{\text{Ga}}^+$ pairs [18].

Table II.

Sample number	$N_D - N_A$	μ_{300}	μ_{77}	As/Ga	T_D	$K = \frac{N_A}{N_D} (*)$
03-044 annealed	2×10^{16}	3 500	14 800	74	680 °C	0.3
	2.6×10^{16}	1 660	4 280	—	—	0.9

(*) Estimated from reference 9.

Heat treatment of GaAs grown by MOVPE was done under $\text{AsH}_3 + \text{H}_2 (P_{\text{AsH}_3} = 10^{-2} \text{ atm.})$ at 750 °C for one hour. Afterwards the electrical properties (table II) were measured and photoluminescence spectra made.

From these results, it appears that the compensation ratio increases after AsH_3 heat treatment by creation of new acceptors or formation of complexes involving V_{Ga} or As_i with existing donors.

3. Photoluminescence data.

3.1 DONOR AND ACCEPTOR SPECTROSCOPY. — Photoluminescence spectra were performed at 1.6 or 4.2 K for some typical samples. The main experimental parameters were T_D and As/Ga. The spectra consist essentially of two groups of lines, the group of bound exciton lines near the band gap and another group of lines corresponding to donor-acceptor and conduction band-acceptor transitions.

The figure 8 (a, b) shows spectra taken at 1.6 K on of 15 at different temperatures, 630 and 730 °C respectively. The main residual acceptors are C and Zn. The peak at 1.492 eV corresponds to the C acceptor-

free electron recombination (C^0, e) and the one at 1.490 eV to the donor-acceptor pair recombination (C^0, D^0) [22]. On the sample grown at 630 °C a peak at 1.487 eV appears, it corresponds to (Zn^0, e) recombination [23] (on some detailed spectra, not reported here, Mg related peaks appeared too). For the sample grown at 730 °C, near band gap excitonic complexes (A^0, X) at 1.512 eV and (D^+, X) or (D^0, h) at 1.513 6 eV are observed.

This result is consistent with an increase of the incorporation of C_{Ga} (or Si_{Ga}) donor with the deposition temperature together with the ratio $C_{\text{Ga}}/C_{\text{As}}$, in agreement with mobility data (table I). C and Zn are the main acceptor impurities in both samples.

On figure 9 (a) and (b) are shown the PL spectra of two samples grown respectively at 630 °C, As/Ga = 7.5 and 630 °C, As/Ga = 37. The first one exhibits broad acceptor related bands (D^0, Zn^0) at 1.486 eV and (D^0, C^0) at 1.490 eV, together with a near band gap peak centered on (A^0, X) at 1.512 eV. The sample grown at 680 °C shows a donor acceptor band (D^0, C^0) at 1.492 eV and a shoulder at 1.488 eV probably due to Zn as in the former spectrum (the shift toward higher

Fig. 8. — Photoluminescence spectra at 1.6 K for two GaAs samples grown at constant As/Ga = 15 ratio at 630 (a) and 730 °C (b) respectively.

Fig. 9. — PL spectra at 4.2 K for two GaAs samples grown at (a) 630 °C, As/Ga = 7.5; (b) 680 °C, As/Ga = 37.

energies is due to an increase of donor concentration). The near band gap peak is centred at 1.514 eV, which corresponds to unresolved donor related transitions (D^0 , X) and (D^0 , h) or (D^+ , X). The compensation ratio of this sample is 0.24. As discussed earlier, the incorporation of C_{Ga} or Si_{Ga} donors is enhanced by high values of the As/Ga ratio.

3.2 DETAILED PHOTOLUMINESCENCE DATA. — On figure 10 (a, c) are shown on a log scale the 4.2 K spectra of three GaAs samples grown at 680 °C with three different As/Ga ratios, respectively 15, 37 and 74.

The main features are, as already discussed, a broad acceptor band (C^0 , D^0), (C^0 e) around 1.490 eV, with its LO phonon replica, and near band gap transitions which can be resolved in figure 10 (b) into structures corresponding to (A^0 , X) (1.512 eV), (D^0 , h) (1.513 eV) and (D^0 , X) (1.514 eV). The high residual concentration $N_A + N_D \simeq 10^{16} \text{ cm}^{-3}$ explains the broadening of the peaks.

For high As/Ga ratios, a shoulder appears at the low energy side of the (D^0 , C^0) band in the range 1.477 to 1.479 eV [27]. In order to clarify the origin of this luminescence band, we have performed annealing experiments under AsH_3 and observed the subsequent modifications of the luminescence spectra. Figure 11 shows that heat treatment of samples under AsH_3 results in an enhancement of the 1.477 eV band by several orders of magnitude.

Photoluminescence spectra of samples grown with excess CH_4 in the gas phase are shown on figure 12. The main features are the following :

— Sample (a) prepared at 680 °C, As/Ga = 15, $P_{CH_4} = 7.5 \times 10^{-4} \text{ atm}$. $n = 1.5 \times 10^{16} \text{ cm}^{-3}$; $\mu_{77} = 17\,700 \text{ cm}^2/\text{V.s}$.

We note that the 1.477 eV shoulder is present.

— Sample (b) prepared at 680 °C, As/Ga = 15, $P_{CH_4} = 10^{-2} \text{ atm}$. $n = 2.5 \times 10^{16} \text{ cm}^{-3}$; $\mu_{77} = 13\,000 \text{ cm}^2/\text{V.s}$.

Increasing P_{CH_4} results in highly compensated samples, whereas the intensity of the 1.477 eV peak shows a slight increase with respect to sample (a).

A tentative origin of this PL band has been proposed [26] : redistribution of C among lattice sites during heat treatment under excess AsH_3 or growth under excess CH_4 and subsequent formation of C_{Ga} - C_{As} complexes. Further investigations on the temperature dependence of this 1.477 eV peak leads us to consider another possibility. First, the coulombic attraction between first neighbours ionized donor and acceptor is large, and the Stokes shift is expected to be large (larger than for $V_{Ga}C_{Ga}$ complexes) although bonding between atoms in GaAs is more covalent than ionic. On figure 13, is presented the temperature dependence of the ratio I_1/I_2 of the intensities of the 1.477 eV band, to the near band gap band (same sample as Fig. 11b). The insert shows that the Full Width Half Maximum (fwhm) of the 1.477 eV band roughly follows a $1.8 kT$ law, which is typical of a free to free

Fig. 10. — PL spectra (intensity on a log scale) for three samples grown at 680 °C, (a) As/Ga = 15; (b) 37; (c) 74.

Fig. 11. — PL spectra at 4.2 K of GaAs sample grown at with, (a) As/Ga = 74 and (b) As/Ga = 37, then annealed one hour at 750 °C under $AsH_3 + H_2$.

Fig. 12. — PL spectra at 2.5 K of sample grown with excess CH_4 . $T_D = 680 \text{ °C}$, As/Ga = 15. (a) $P_{CH_4} = 7.5 \times 10^{-4}$, (b) $P_{CH_4} = 10^{-2} \text{ atm}$.

Fig. 13. — Temperature dependence of the ratio (sample 11b) of the intensities of the 1.477 eV band (I_1) to the near gap emission band (I_2). The insert shows a comparison of the

with the expected behaviour of free to bound (or free to free) transition.

or free to band transition. Assuming then that free electrons are involved in the 1.477 eV band, the ratio I_1/I_2 is proportional to the ratio of the population of holes on a level at energy E_A to the population of holes in the valence band. Under low excitation and at sufficiently high temperature, we can assume Boltzmann's statistics

$$I_1/I_2 \propto \exp\left(-\frac{E_A}{kT}\right).$$

The data on figure 13 then shows that the 1.477 eV band arises from the recombination of a free electron with $a = 37$ meV deep acceptor. Note that, due to the broadening of the spectra in compensated materials such as those obtained after AsH_3 annealing, the value of E_A is to be considered as an estimate. However, the agreement between optical (≈ 41 meV) and thermal (≈ 37 meV) activation energy is satisfactory.

Substitutional germanium on an As site is known to give rise to a 40.5 meV deep acceptor [27]. We discard the possibility of Ge contamination for three reasons :

i) Under AsH_3 annealing (or growth under high AsH_3 overpressures) Ge is expected to transfer from As to Ga sites, which would result in a decrease of the Ge acceptor bands, together with a decrease in compensation in n type samples (see Fig. 6). The inverse is in fact observed.

ii) The same argument holds for samples grown with excess CH_4 in the gas phase. Indeed, from equation 6, a decrease of Ge incorporation on As sites is expected, whereas compensation and 1.477 eV PL intensity show an increase.

iii) Lastly, SIMS analysis (CAMECA SMI 300) did not reveal the presence of Ge impurities in the samples studied, although we are aware that Ge is hard to distinguish from Ga in mass spectroscopy.

To this point, as this acceptor PL peak does not seem to originate from any commonly known substitutional impurity [25], only conjectures can be made from our results. We note first that this acceptor may be carbon related, as it appears together with the presence of excess CH_4 in the gas phase. Second, it can also be related with defect appearing with an excess As (or a Ga deficiency, as from figure 5, AsH_3 or CH_4 overpressures have the same effect on the stoichiometry of the growing crystal).

The large number of non stoichiometry defects that can exist in a III-V compound prevents further identification. A more detailed study of this acceptor would require more resolved PL spectra, i.e. purer samples, but we note that this PL band appears in

leading to large residual impurities concentrations (AsH_3 annealing or introduction of CH_4 in the gas phase).

On the other hand, it has to be noted that PL peaks appear in the 1.47-1.49 eV range in high purity MBE samples, that have also been correlated with C and stoichiometry defects [26, 27].

4. Conclusions.

The main problem that remains in MO-VPE is the incorporation of C. C is incorporated as both donor and acceptor. It probably results from the partial pyrolysis of CH_4 . This was shown by experiments with excess CH_4 in the gas mixture. The amounts of C can be decreased when growing layers at the lowest possible temperature, and under low pressure vapour phase epitaxy.

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