

GaAs METAL ORGANICS VAPOUR PHASE EPITAXY : RESIDUAL CARBON

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RESUME

Les couches de GaAs élaborées à partir de triméthylgallium (TMG) et d'Arsine (AsH_3) contiennent du carbone résiduel qui s'incorpore essentiellement sous forme d'accepteur. Les spectres de photoluminescence présentent en dehors des faits habituels un pic à 1.477 eV, qui est d'autant plus intense que le rapport As/Ga dans la phase vapeur est élevé. Un recuit sous mélange $\text{H}_2 + \text{AsH}_3$ augmente l'intensité de ce pic. Des couches de GaAs ont été élaborées avec un excès de CH_4 . Ceci donne des couches très compensées. Le pic à 1.477 eV existe dans tous ces échantillons. La cinétique de croissance est profondément modifiée par l'excès de méthane.

ABSTRACT

GaAs grown from trimethylgallium (TMG) and arsine (AsH_3) containing residual carbon. It is mostly incorporated essentially as acceptor. Photoluminescence spectra exhibit besides the usual features a peak at 1.477 eV the higher the greater the ratio As/Ga. Annealing under $\text{H}_2 + \text{AsH}_3$ enhances the intensity of this peak. GaAs layers were grown with excess CH_4 . This gives highly compensated layers; the 1.477 eV peak appears in all these samples. The kinetics of growth is drastically changed by the excess CH_4 .

1 - INTRODUCTION

MO-VPE had become a widely used method for growing GaAs epitaxial layers with electronic quality equalling that obtained in the Ga - AsCl_3 - H_2 method.

Residual carbon impurities $< 10^{15} \text{ cm}^{-3}$ are always found in MO-VPE GaAs from TMG and AsH_3 . This residual carbon gives an acceptor peak in photoluminescence (PL) spectra. Its density was measured by nuclear activation.

In 1975, Seki (1) using TEG instead of TMG obtained high mobility GaAs. His GaAs was almost free of C. He explained his results assuming that no Ga-C-Ga bond could be formed during the pyrolysis process: (In the case of TMAI, Al-C-Al bridges do exist and Al_4C_3 may be obtained. To avoid the formation of carbide in growing AlSb, triisobutylaluminium was used as aluminium source (2). It has been argued too (3) that contaminants may be responsible for the carbon pollution).

Recently Bhat (4) grew high purity GaAs from TMG or TEG sources. He got high mobility samples $\sim 10^5 \text{ cm}^2/\text{V}\cdot\text{sec}$ in GaAs grown from TEG. PL spectra did not show any carbon acceptor peak.

Experiments reported here deal with some aspect of C contamination. Emphasis was put on detailed PL spectra on samples grown under different conditions. Heat treatment under $\text{AsH}_3 + \text{H}_2$ was done on specific samples in order to change the native defects equilibrium, thus the incorporation of carbon either in As or Ga site. Some layers were grown with excess CH_4 in the gas phase. These preliminary results show that, the extra CH_4 as well as CH_4 arising from the thermal decomposition of TMG, is to some extent incorporated in the growing GaAs layers.

2 - EXPERIMENTAL

2.1.1 - GaAs layers from TMG and AsH_3

We checked - as most the authors involved in this field did - that v_g the speed of deposition is independent of T_D the deposition temperature (between 600 and 750°C), of P_{AsH_3} and is proportional to P_{TMG} . The nature of the residual impurities depends on the ratio As/Ga in the vapour phase. Depending on As/Ga p or n type layers are obtained.

2.1.2 - Photoluminescence spectra

Fig. 1 shows on a log scale 4.2K PL spectra of three different samples grown at 680°C, with As/Ga = 15, 37, 74 respectively. Besides the usual peaks, i.e. excitonic features near the band gap ; (C°, e) peak at 1.493 eV (6), LO replica 36 meV below, the spectra show for high As/Ga values a shoulder about 1.477eV. This peak is greater the higher the As/Ga ratio.

This peak is usually assigned to Ge acceptor. However SIMS analysis does not show any trace of Ge. Furthermore the incorporation of Ge acceptors Ge_{As}^- ($\propto P_{\text{AsH}_3}^{-1}$) should decrease with increasing P_{AsH_3} . This is not the case. There is yet no formal assignment for this peak.

2.1.3 - Annealing

Annealing under $\text{H}_2 + \text{AsH}_3$ (10^{-2} atm) during one hour at 680°C was carried out on samples grown with As/Ga = 37 and 74. An increase of V_{Ga} results from this heat treatment ; this allows the redistribution of C_{As} towards Ga site and possibly the formation of $C_{\text{As}}^- - C_{\text{Ga}}^+$ complexes. In highly doped Si - GaAs, heat treatment under partial pressure of AsH_3 results in redistribution of Si among As and Ga sites and in the formation of $\text{Si}_{\text{As}}^- - \text{Si}_{\text{Ga}}^+$ complexes (7).

For a typical sample grown at 680°C, with $\frac{\text{As}}{\text{Ga}} = 37$, $\mu_{300} = 3500 \text{ cm}^2/\text{V}\cdot\text{sec}$, $N_D - N_A = 2.10^{16} \text{ cm}^{-3}$ ($K = 0.8$). After annealing, $N_D - N_A = 2.6.10^{15} \text{ cm}^{-3}$ whereas $\mu_{300} = 1660 \text{ cm}^2/\text{V}\cdot\text{sec}$. The conversion of C_{As} into C_{Ga} and the formation of some kind of complex like $C_{\text{As}}^- - C_{\text{Ga}}^+$ is consistent with these data.

On the PL spectra of annealed samples, the height of the 1.477eV peak increases by several orders of magnitude (Fig.2).

2.2 - MO-VPE of GaAs with excess of CH_4 in the gas phase

An excess of CH_4 in the input gases H_2 , TMG, AsH_3 results in decreasing the speed of deposition V_g . V_g experimentally verifies the law $V_g \propto P_{\text{CH}_4}^{-0.3}$ at a given temperature (680°C) (Fig. 3). Furthermore at constant As/Ga, V_g is temperature dependent.

For $T > 630^\circ\text{C}$, V_g is thermally activated (Fig. 4)

$$V_g \propto \exp - E_a/KT \text{ with } E_a \approx 26 \text{ Kcal.}$$

In standard conditions $T = 680^\circ\text{C}$, $\text{As/Ga} = 15$ a typical sample shows the following properties

$$N_D - N_A \approx 10^{15} \text{ cm}^{-3}, \mu_{77} \approx 3.10^4 \text{ cm}^2/\text{Vsec}$$

with an excess CH_4 , $P_{\text{CH}_4} = 10^{-2} \text{ atm}$

$$N_D - N_A = 2.10^{16} \text{ cm}^{-3}, \mu_{77} = 1.3.10^4 \text{ cm}^2/\text{Vsec}$$

These results show that C is incorporated both as donor and acceptor. (It is roughly verified over five runs that $N_D \propto P_{\text{CH}_4}^{-3}$, $N_A \propto P_{\text{CH}_4}^{-2}$).

The PL spectra of these samples are shown on Fig. 5. The main peaks are present as usual (C° , e) overlapping (C° , D°) ; (A° , X), (D° , X). However the (A° , X) peak, corresponding probably to C_{As} in higher than in standard samples grown without CH_4 . This peak is to be related to C to some form to be hypothesized.

2.3 - Other results

GaAs grown from TEG do not present carbon contamination (1, 4). The 1.493 (C° , e) acceptor peak does not exist in PL spectra. On the other hand GaAs prepared from TMG and trimethylarsenic (TMAs) (instead of AsH_3) shows poor mobilities $\mu_{300} \approx 3500 \text{ cm}^2/\text{Vsec}$. GaAs grown from TMG and TMAs is formed by the simultaneous pyrolysis of TMG and TMAs. This brings CH_4 molecules in the gas phase and finally similar features than GaAs grown with excess CH_4 are observed, i.e, highly compensated samples, broad acceptor peaks in PL spectra (C° , e) and probably other acceptor impurities, the speed of deposition decreases with increasing As/Ga (or with increasing partial pressure of CH_4 in the gas phase).

It must be emphasized that in these both examples, no add compounds are formed.

3 - PRIMARY ANALYSIS OF THE DATA

3.1 - PL peak at 1.477eV

It was already shown that this peak is not due to Ge acceptor and this was discussed recently by Hess et al too (8). A plausible explanation of all the observed features is the existence of some complex, possibly $\text{C}_{\text{As}}^- - \text{C}_{\text{Ga}}^+$. The heat treatment under AsH_3 causes outdiffusion of V_{Ga} then results in the redistribution of C among As and Ga site, and increases the $\text{C}_{\text{As}} - \text{C}_{\text{Ga}}$ density (observed by the enhancement of the 1.477eV peak)*. The slight difference between calculated and measured energy can be attributed to the Stokes shift. Preliminary results on the temperature behaviour of this luminescence peak do not seem to indicate an electron to acceptor type peak. Further experiments is anyhow still needed.

* The distribution of C on the two sublattices varies with the concentration of C.

3.2 - Kinetics data

It is assumed in standard MO-VPE experiments that the speed of deposition is limited by mass transfert through a boundary layer. The speed is directly proportionnal to P_{TMG} . The addition of extra CH_4 changes the nature of kinetics towards a surface limited process (Fig. 4).

Schlyer (9) showed that TMG and AsH_3 form an add compound $Ga(CH_3)_3 - AsH_3$. Around 200 - 250°C this add compound loses CH_4 molecules to give $Ga(CH_3)_{3-x}AsH_{3-x}$ complexes. The addition of extra CH_4 changes the equilibrium of formation of this complexe, and the kinetics of its decomposition into GaAs.

4 - FURTHER DEVELOPMENTS - Suggestions

A direct proof of the incorporation of carbon in GaAs from CH_4 molecules (and from other carbon source or some Ga - C - Ga bridge) can be brought by EPR using ^{13}C .

^{13}C exhibits an hyperfine field whereas ^{12}C does not, EPR is a good tool to recognize ^{13}C in GaAs.

An in situ method to investigate the gas phase is of great importance to define the temperature profile and the composition of the gas phase. For instance. Raman spectroscopy, more precisely CARS (coherent antistroke Raman spectroscopy) A laser beam is scanned along a normal to the substrate and the Raman signal is analyzed. Preliminary experiments in closed tubes show that TMG and AsH_3 exhibit well defined Raman spectra. Add complexes like the one described by Schlyer $Ga(CH_3)_{3-x}AsH_{3-x}$ are expected to be identified.

5 - CONCLUSION

A better understanding of the chemistry and aerothermochemistry in MO-VPE is urgently needed to improve the quality of the layers. A non destructive, and non intrusive method like in situ Raman spectroscopy should prove to be very helpful.

ACKNOWLEDGMENTS

The authors wish to express their thanks to M. GUITTARD for helpful experimental support and R. DRUILHE for some unpublished results. This work was supported by DAIJ under contract 80-35-009.

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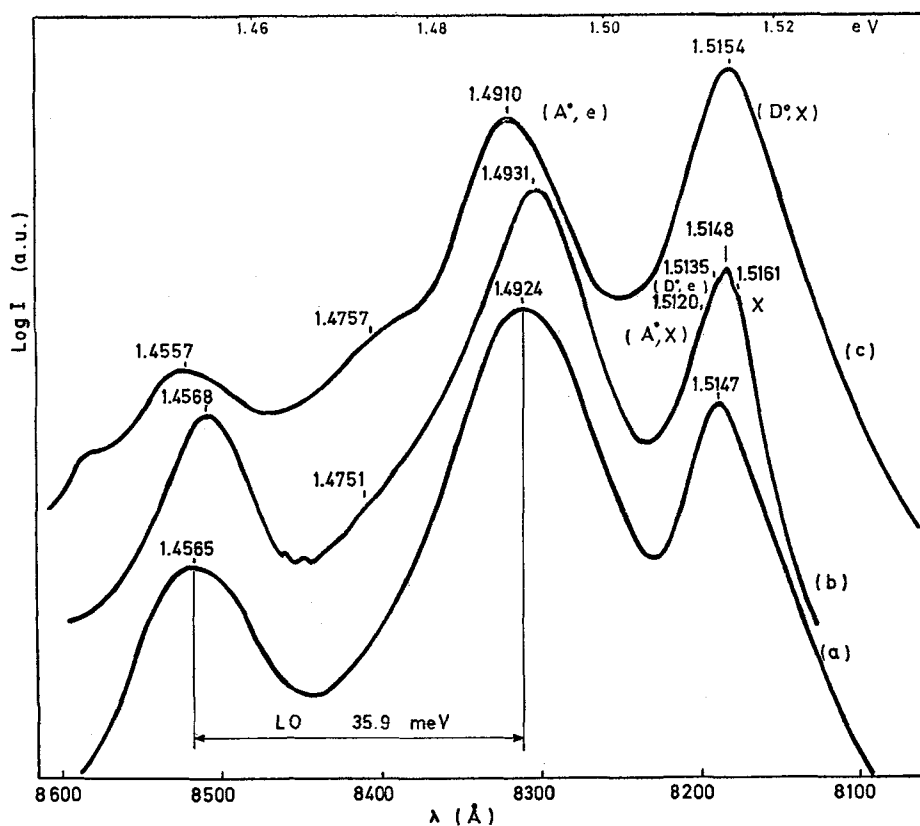


FIGURE 1

Photoluminescence spectra at 4.2 K (Log Scale) of three OM-VPE samples grown at 680°C with (a) As/Ga = 15, (b) 37 and (c) 74 respectively

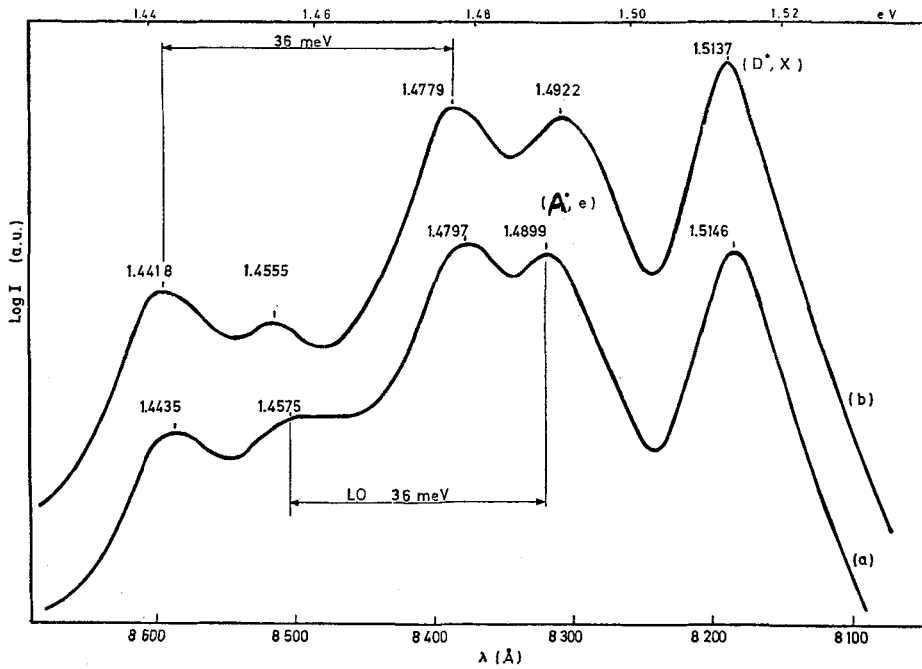


FIGURE 2

Photoluminescence spectra at 4.2 K (Log Scale) on samples grown at 680°C, annealed one hour under AsH_3 (10^{-2} atm) + H_2
 (a) $\frac{\text{As}}{\text{Ga}} = 74$ (b) $\text{As/Ga} = 37$

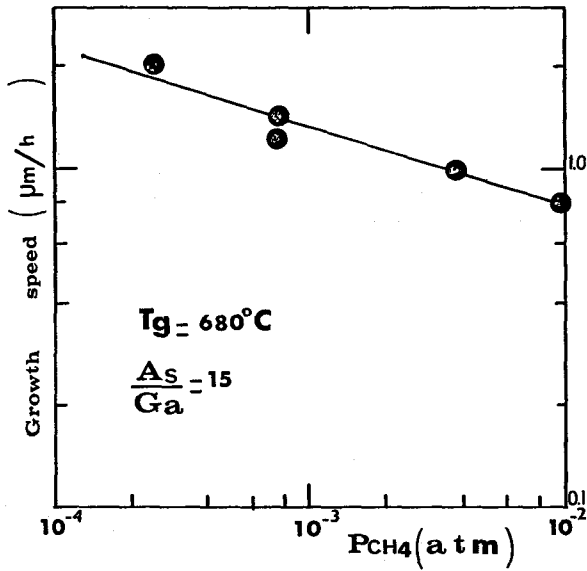


FIGURE 3

Speed of deposition of MO-VPE GaAs grown with excess CH₄ (As/Ga = 15, T₀ = 680°C) as a function of the partial pressure of excess CH₄

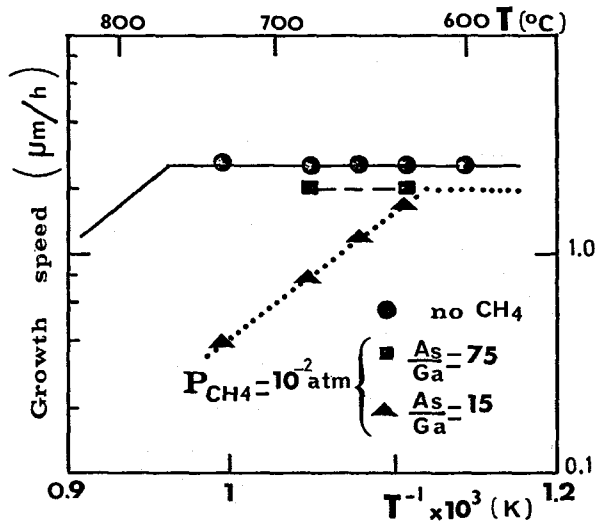


FIGURE 4

Speed of deposition of MO-VPE GaAs grown with excess CH₄ as a function of 1/T

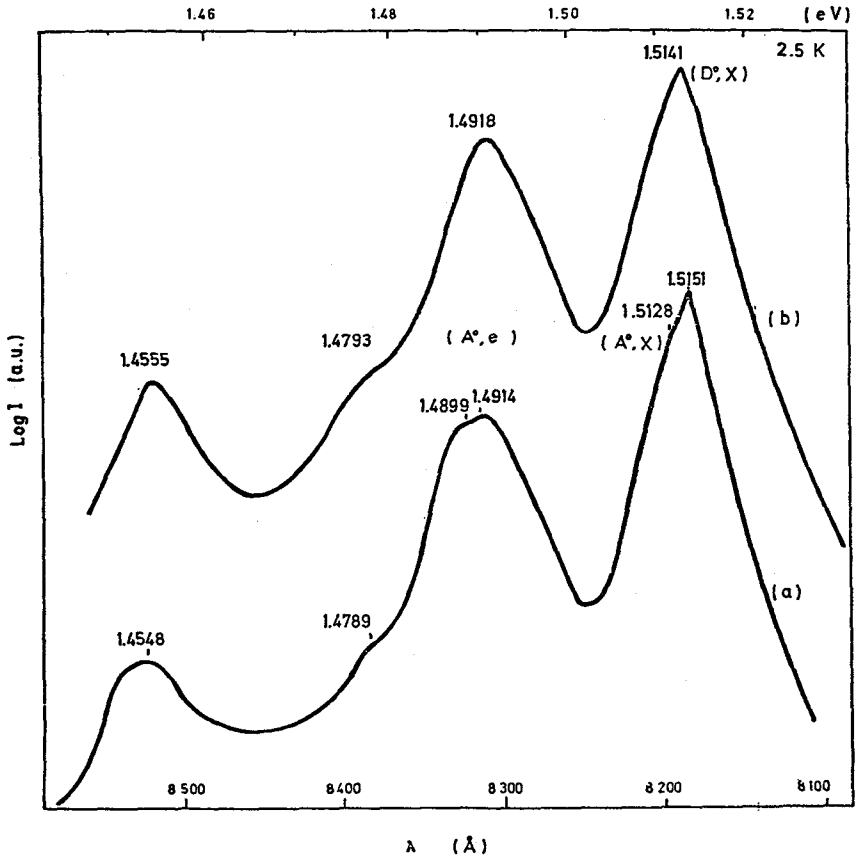


FIGURE 5

Photoluminescence spectra at 4.2 K (Log Scale) of MO-VPE GaAs samples grown at 680°C, As/Ga = 15 with excess CH_4
 (a) $P_{CH_4} = 7.5 \cdot 10^{-4}$ atm (b) $P_{CH_4} = 10^{-2}$ atm