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Metal organics vapour phase epitaxy of GaAs : Raman studies of complexes formation

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Résumé. — Le remplacement de l'arsine par le triméthylarsenic (TMAs) lors de l'épithaxie en phase vapeur à partir d'organométalliques (EPVOM) de GaAs conduit à des matériaux ayant un résiduel élevé ($\sim 10^{17} \text{ cm}^{-3}$). La spectroscopie Raman montre qu'il se forme un solide relativement stable entre le triméthylgallium (TMG) et l'arsine, alors qu'il ne s'en forme pas entre TMG et TMAs. Ce fait pourrait expliquer l'incorporation élevée de carbone lors de l'EPVOM de GaAs en utilisant TMAs.

Abstract. — The use of trimethylarsenic (TMAs) in place of arsine in metal organics vapour phase epitaxy (MOVPE) of GaAs gives samples with high residual doping ($\sim 10^{17} \text{ cm}^{-3}$). Raman spectroscopy shows that a rather stable solid is formed between trimethylgallium (TMG) and AsH_3 , whereas no adduct is formed between TMG and TMAs. This feature could explain the high density of residual carbon when using TMAs in MOVPE of GaAs.

Introduction.

Metal organics vapour phase epitaxy (MOVPE) has proved to be a suitable method to grow electronic quality GaAs and to manufacture GaAs devices including solar cells, diode lasers, QW structures, superlattices...

GaAs epilayers grown by MOVPE from $\text{Ga}(\text{CH}_3)_3$ (TMG) and AsH_3 exhibit reliable electronic properties. With high purity starting AsH_3 and redistilled $\text{Ga}(\text{CH}_3)_3$ several groups [1, 2] reached $150\,000 \text{ cm}^2/\text{V.s}$ for μ_{77} with a residual concentration of impurities $N_D - N_A \sim 10^{14} \text{ cm}^{-3}$.

Beside TMG and AsH_3 , other metal organics could be used :

- $\text{Ga}(\text{C}_2\text{H}_5)_3$ (TEG) [3, 4]
- $(\text{CH}_3)_3\text{GaO}(\text{C}_2\text{H}_5)_2$ or $\text{Ga}(\text{C}_2\text{H}_5)_2\text{Cl}$
- $\text{As}(\text{CH}_3)_3$ [6, 7] or $\text{As}(\text{C}_2\text{H}_5)_3$ [6].

Even complex molecules, such as GaAsEt_5Cl [8], containing both Ga and As atoms could be successfully used to grow GaAs epilayers. The nature of the

residual impurities is dominated both by the purity of the starting metalorganic and the nature of the process involved in the pyrolysis. In other words, residual impurities could result from one atom of the starting molecules (i.e. C from the CH_3 group or Cl from halides). Reaction mechanisms in MOVPE are not known in details yet. Mass spectrometry [10] and infrared spectroscopy [11, 12] were used to analyse, *in situ*, the gas phase composition in a MOVPE reactor.

1. GaAs from TMG and AsH_3 .

1.1 RESIDUAL CARBON. — Zn, Si, and C are the most common among residual impurities in MOVPE GaAs epilayers grown from TMG and AsH_3 .

C is unambiguously identified in photoluminescence spectra by two specific peaks : a (e , C^0) recombination peak at 1.4934 eV and a (D^0 , C^0) at 1.490 eV (Fig. 1a). Another peak at 1.479 eV was found in PL spectra of GaAs grown with large As/Ga ratio (~ 30) or with excess CH_4 . This peak was assigned to carbon acceptor in an unidentified form [9].

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Fig. 1. — 4.2 photoluminescence spectra of GaAs grown by MOVPE from TMG and AsH₃ (a); TMG and As(CH₃)₃ (b). The sample (a) was prepared at 630 °C, with As/Ga = 10, $P_{\text{TMG}} = 8.5$ Pa. The residual concentration of impurities was $N_D - N_A = 4 \times 10^{14} \text{ cm}^{-3}$ with $\mu_{77\text{K}} = 40\,000 \text{ cm}^2/\text{V.s.}$ The spectrum (a) exhibits well defined near band gap excitonic complexes : 1.5156 eV (FE), 1.5137 (D⁰, X), 1.5133 (D⁰, h), 1.5122 (A⁰, X) and 1.5108 eV, g exciton. Furthermore the PL spectra show two peaks associated to carbon acceptors : 1.4932 eV (D⁰, C⁰) and 1.4908 (e, C⁰) recombination. The sample (b) was prepared at 630 °C, with As/Ga = 10, $P_{\text{TMG}} = 12.6$ Pa. The free donor concentration was $1.4 \times 10^{17} \text{ cm}^{-3}$ with $\mu_{300\text{K}} = 3\,100 \text{ cm}^2/\text{V.s.}$ The near band gap peak is broad and very weak. The mean feature of this spectrum is the huge broad acceptor peak, (D⁰, C⁰) and (e, C⁰) are not separated, the broadening of these recombination peaks is due to the high density of residual carriers. The two PL spectra were chosen to compare GaAs layers grown with the same As/Ga ratio, at the same temperature. However, in MOVPE of GaAs from TMG and As(CH₃)₃, better spectra were obtained with As/Ga = 2 [17] whereas starting from TMG and AsH₃ the best layers were grown using As/Ga = 25.

1.2 GaAs GROWTH WITH EXCESS CH₄. — Excess CH₄ in the vapour phase results in the growth of compensated samples. C is probably incorporated both as donors and acceptors. Besides the usual (e, C⁰) and (D⁰, C⁰) recombination peaks, PL spectra show an enhanced peak at 1.479 eV [9]. Furthermore the addition of CH₄ changes the growth velocity. For $P_{\text{CH}_4} \gtrsim 10$ Pa the growth process becomes kinetically controlled [9].

1.3 INCORPORATION OF C IN GaAs. — C in MOVPE GaAs arises from methyl radicals. Several elementary processes can be hypothesized :

- incorporation of C from adsorbed CH₄ molecules (TMG decomposes into CH₄);
- formation in the gas phase of an adduct Ga(CH₃)₃-AsH₃ and decomposition at the substrate of this adduct;
- decomposition of Ga(CH₃)₃ into GaCH₃ and adsorption of CH₃ radicals at As sites [10].

At this point in time no direct answer is evident. A non intrusive, non destructive method of *in situ* investigation is needed for a better understanding of the processes involved in the pyrolysis of TMG and AsH₃. Raman spectroscopy can give direct information about the nature and concentration of gaseous species. As a preliminary study of processes involved in MOVPE by *in situ* Raman spectroscopy, we studied the thermal behaviour of Raman spectra of TMG, AsH₃, TMAs and mixtures TMG-AsH₃, TMG-TMAs which were kept in closed silica cells.

1.4 THERMAL DEPENDENCE OF RAMAN SPECTRA OF TMG, AsH₃ AND TMG + AsH₃.

1.4.1 TMG. — The Raman spectrum in gas phase of Ga(CH₃)₃ at 100 °C is presented in figure 2. Ga(CH₃)₃ which is monomeric in the gas phase with a planar

Fig. 2. — Raman spectrum of TMG at 100 °C.

GaC₃ skeleton, belongs to the point group D_{3h}. Therefore the vibrational assignments are :

$$\delta_{\text{d(Ga-C)}(\text{E}') = 146 \text{ cm}^{-1}$$

$$\nu_{\text{s(Ga-C)}(\text{A}') = 521 \text{ cm}^{-1}$$

$$\nu_{\text{d(Ga-C)}(\text{E}') = 562 \text{ cm}^{-1}.$$

The other bands arise from motions of the methyl groups

$$\delta_{\text{s(C-H)}} = 1\,204 \text{ cm}^{-1}$$

$$\nu_{\text{d(C-H)}} = 2\,907 \text{ cm}^{-1}$$

$$\nu_{\text{s(C-H)}} = 2\,914 \text{ cm}^{-1}.$$

TMG starts to decompose at about 250 °C. This gives only CH₄, no H₂ and there were no other hydrocarbons detected.

1.4.2 AsH₃. — AsH₃, with symmetry C_{3v}, gives four bands :

$$\nu_{\text{s(As-H)}(\text{A}_1) = 2\,114 \text{ cm}^{-1} \text{ (strong)}$$

$$\nu_{\text{d(As-H)}(\text{E}) = 2\,126 \text{ cm}^{-1} \text{ (medium)}$$

$$\delta_{\text{s(As-H)}(\text{A}_1) = 990 \text{ cm}^{-1} \text{ (weak)}$$

$$\delta_{\text{d(As-H)}(\text{E}) = 898 \text{ cm}^{-1} \text{ (")}.}$$

AsH₃ is stable up to 150 °C. At higher temperatures, H₂ will appear and at 400 °C, AsH₃ is completely decomposed into As₄ and H₂.

1.4.3 TMG + AsH₃. — Raman cells are first filled with TMG, then cooled down to liquid nitrogen temperature. Afterwards AsH₃ is added and the cell sealed off. Several mixtures were made around the stoichiometric composition 1 : 1.

When mixing TMG and AsH₃ even as low as to 1 013 Pa, a white solid is formed that decomposes under laser impact. This solid is stable enough to be isolated, but looks inhomogeneous and its colour becomes yellow with time. The results of the microanalysis are (weight %) :

$$\begin{array}{ll} \text{Ga} = 51.44 \% & \text{As} = 36.44 \% \\ \text{C} = 10.07 \% & \text{H} = 2.77 \%. \end{array}$$

This solid is slowly formed from a liquid phase after spontaneous separation of gas phase. The Raman analysis of the gaseous phase above the solid gives CH₄.

Then the bulk reaction which occurs may be written :

This solid may be a mixture, it is also possible that a slow polymerization process may take place and it is very moisture sensitive.

Raman [13] and I.R. spectra [14] (Figs. 3a-b) of this solid has been recorded. Vibrational assignments are

Fig. 3a. — Raman spectrum of the solid obtained in closed cells from TMG and AsH₃, temperature of the cell 100 °C.

Fig. 3b. — IR spectrum of this solid.

difficult to assess for this solid (Table I). The only certainty is the existence of a band for the Ga-As bond at 266 cm^{-1} , since for GaAs we have found the same value for $\nu_s(\text{GaAs})$.

Table I. — *Observed spectra of solid (TMG + AsH₃).*

Raman (solid)	Infrared (CsBr, pellet)	Assignments
266	255	$\nu_{(\text{Ga}-\text{As})}$
521	—	
	595	$\nu_{(\text{Ga}-\text{C})}$
	735	
	995	
1 145	1 215	$\delta_{(\text{C}-\text{H})}$
1 202		
	1 410	
	1 465	
	2 110	$\nu_{(\text{As}-\text{H})}$
2 906	2 910	$\nu_{(\text{C}-\text{H})}$
2 968	2 965	

The decomposition of this solid was deduced from the temperature dependence of Raman spectra of gases in equilibrium with the solid. Decomposition starts at 350°C and CH_4 is the only gas which comes from the decomposition of the solid. This was not the behaviour reported by Ring and Schlyer [15]. However, the experimental conditions were different. In their experiment the reaction occurred in contact with GaAs and at higher temperature, the complex formed was probably different.

The main feature deduced from the present Raman studies is the existence of (a) rather stable solid compound(s) formed between TMG and AsH_3 . This solid results from the mixing of TMG and AsH_3 by elimination of CH_4 molecules. These results cannot be — of course — directly extrapolated to reactions occurring in the gas phase. Anyhow recent studies have shown that AsH_3 decomposition is enhanced by TMG addition [10, 11]. In the vapour phase the adduct is likely formed or some intermediate complex formed by the elimination of CH_4 molecules and the incorporation of carbon occurs *via* the incomplete desorption of CH_3 groups at the interface. These CH_3 groups may belong to Ga-As- CH_3 complexes [16].

2. GaAs from TMG and $\text{As}(\text{CH}_3)_3$ (TMAs).

AsH_3 can be replaced by $\text{As}(\text{CH}_3)_3$ in MOVPE of GaAs. The danger of using highly poisonous AsH_3 is somewhat reduced when using the rather stable metalorganic $\text{As}(\text{CH}_3)_3$. Moreover, using TMAs may overcome the problem of formation of stable adducts when growing In compounds. GaAs layers were grown from TMG and TMAs. The main growth parameters

were deposition temperature and the ratio As/Ga in the gas phase, partial pressure of TMG. Some experiments were carried out at reduced pressure.

2.1 RESIDUAL DOPING. — Whatever the ratio As/Ga (in the range 2-40) all other growth conditions kept constant : $T_D = 630^\circ\text{C}$, operating pressure 10^5 Pa , total H_2 flow 5 l/min, $P_{\text{TMG}} = 12.6\text{ Pa}$, the residual doping remains high : $N_D - N_A \sim 2 \times 10^{17}\text{ cm}^{-3}$, $\mu_{300} \sim 3\,000\text{ cm}^2/\text{V.s}$ and the compensation ratio is about 0.6. This means that donor and acceptor impurities are incorporated at densities of the order of $2\text{--}4 \times 10^{17}\text{ cm}^{-3}$. The most likely acceptor impurity is C. As in the TMG- AsH_3 standard method N_D and N_A increases with T_D and the ratio As/Ga. Low pressure deposition results in even higher residual doping levels [17].

The 4.2 K PL spectra show unsolved features near the band edge together with very broad acceptor peaks (Fig. 1b).

2.2 THERMAL DEPENDENCE OF RAMAN SPECTRA OF TMAs AND TMG + TMAs. — $\text{As}(\text{CH}_3)_3$ with a supposed AsC_3 skeleton has the point group C_{3v} . Therefore the vibrational assignments are :

$$\begin{aligned}\delta_{\text{d}(\text{As}-\text{C})[\text{E}]} &= 230\text{ cm}^{-1} \\ \nu_{\text{s}(\text{As}-\text{C})[\text{A}_1]} &= 570\text{ cm}^{-1} \\ \nu_{\text{d}(\text{As}-\text{C})[\text{E}]} &= 590\text{ cm}^{-1}.\end{aligned}$$

Furthermore the bands from the motions of the methyl group are :

$$\begin{aligned}\delta_{\text{s}(\text{C}-\text{H})} &= 1\,260\text{ cm}^{-1} \\ \nu_{\text{d}(\text{C}-\text{H})} &= 2\,907\text{ cm}^{-1} \\ \nu_{\text{s}(\text{C}-\text{H})} &= 2\,914\text{ cm}^{-1}.\end{aligned}$$

TMAs remains stable up to 300°C . A mixture TMG + TMAs (1 kPa) was placed in a sealed quartz cell for Raman analysis. The Raman spectrum (Fig. 4) is just the superposition of the TMG and TMAs spectra (Fig. 4). There is no evidence of adduct formation. Starting from 200°C , the intensities of the above mentioned peaks starts to decrease. No new compound correlatively appears.

2.3 PRELIMINARY CONCLUSIONS. — It is well established that $\text{Ga}(\text{CH}_3)_3$ and $\text{As}(\text{CH}_3)_3$ form an adduct with lower vapour pressure than the constituents [18]. However, in the experimental conditions used in Raman spectroscopy (1 000 Pa, 100°C) the adduct is already dissociated. It can be extrapolated from the present Raman studies that As and Ga atoms are *separately* brought to the growing interface and that CH_4 molecules arising from the decomposition of TMG and TMAs should desorb. The high concentration of CH_3 radicals at the interface is likely a source of C in the layers.

Fig. 4. — Raman spectrum of a mixture TMG and $\text{As}(\text{CH}_3)_3$ (100 °C, 1 kPa). The spectrum is only the superposition of TMG and $\text{As}(\text{CH}_3)_3$ spectra.

3. GaAs from $\text{Ga}(\text{C}_2\text{H}_5)_3$ and AsH_3 .

Published results [3, 4] reported high mobility materials. It was pointed out that carbon incorporation is limited, in low temperature PL spectra (C^0 , D^0) and (e , C^0) recombination peaks do not appear. The pyrolysis of $\text{Ga}(\text{C}_2\text{H}_5)_3$ produces C_2H_6 which prevents C to be incorporated in the GaAs growing layer.

4. Other metal organics.

GaAs grown from unusual metalorganics present a high level of residual impurities : 10^{17} to 10^{18} cm^{-3} . These uncommon metalorganics are not available with « electronic » purity. Furthermore the pyrolysis of these compounds results in the incorporation of atoms belonging to the starting metalorganic : Cl, O, C.

GaAs grown from $\text{GaMe}_2\text{ClAsEt}_3$ or $\text{GaEt}_2\text{ClAsEt}_3$ contains significant amount of carbon as showed by Auger spectroscopy [19].

5. Discussion.

The Raman spectroscopy experiments were carried out in closed cells without H_2 dilution. They cannot be directly extrapolated to real epitaxial systems. In a future extension of this exploratory study, *in situ* Raman spectroscopy will be developed. Anyhow, from these preliminary results the following conclusions can be driven :

— C is incorporated when CH_3 radicals (or CH_4 molecules) are present.

— A stable solid compound is formed between $\text{Ga}(\text{CH}_3)_3$ and AsH_3 (in closed cells down to 1 kPa). A « compound » is likely to be formed in the vapour phase in a MOVPE reactor. Nishizawa *et al.* [11] studied the reaction mechanism of GaAs formation in MOVPE using IR spectroscopy, they pointed out the

existence of a « compound » of unknown composition between TMG and AsH_3 even at concentrations of the order of 10 Pa. On the other hand no stable adduct was evidenced between $\text{Ga}(\text{CH}_3)_3$ and $\text{As}(\text{CH}_3)_3$ in closed cells (down to 1 kPa) and is probably not formed in the gas phase.

— Due to high thermal gradient in the reactor near the susceptor, the « compound » formed in the gas phase between TMG and AsH_3 is probably brought very close to the surface of the substrate before decomposition. In the MOVPE of GaAs from TMG and TMAs, Ga and As atoms are separately brought to the growing interface.

— The incorporation of C in GaAs results from the incomplete desorption of CH_3 radicals. In the case of MOVPE from TMG and AsH_3 , it has been hypothesized that growth occurs *via* As-Ga- CH_3 complexes, this could explain the growth anisotropy [16] and the anisotropic incorporation of carbon atoms [20]. In the MOVPE of GaAs from TMG and TMAs no ternary complex may be formed; growth occurs *via* incorporation of Ga and As atoms separately (or GaCH_3 and AsCH_3 radicals). $\text{As}(\text{CH}_3)_3$ is rather stable metalorganic; the bond strength of As-C in TMAs (55 kcal), can be compared to Ga-C in TMG (59 kcal). A high density of CH_3 radicals bound to the surface results in carbon incorporation to a much greater extend than in the TMG- AsH_3 system.

— Finally, in the MOVPE of GaAs from TEG and AsH_3 no data on stability of the adduct exist. However, TEG decomposes giving C_2H_6 , which cannot be incorporated in the growing layer for steric features. Low temperature photoluminescence spectra of GaAs grown from TEG and AsH_3 do not present (D , A) and (e , A^0) recombination peaks due to carbon [3].

Great progress in the understanding of the MOVPE reaction mechanisms is expected from *in situ* investigation methods like IR, UV or Raman spectroscopy.

In addition, the temperature profile in an MOVPE reactor can be studied by means of rotational Raman scattering of H_2 .

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