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PARAMETRIC STUDIES OF GaAs GROWTH BY METALORGANIC MOLECULAR BEAM EPITAXY

N. Vodjdani, A. Lemarchand and H. Paradan

*Laboratoires d'Electronique et de Physique Appliquée, 3, Avenue Descartes, 94450 Limeil Brévannes, France*Résumé

L'association d'un bâti d'épitaxie par jets moléculaires aux sources gazeuses d'organométalliques employées en croissance en phase vapeur (MOCVD) du GaAs est décrite.

La décomposition thermique de l'arsine (AsH_3) et du triméthylgallium (TMG) ont été étudiées par spectrométrie de masse. L'énergie d'activation apparente de dissociation de l'arsine est évaluée à 35 kcal/mole. La possibilité de croissance épitaxiale de GaAs à partir de TMG pur et d'arsenic élémentaire (As_4) sous ultra vide est démontrée. Les cinétiques de croissance dans les systèmes (TMG, As_4) et (TMG, AsH_3) sont analysées. En particulier le type de mécanisme de croissance mis en jeu a permis de développer une méthode pour effectuer des épitaxies localisées.

Abstract

The combination of the gaseous species of a conventional MOCVD system with a UHV chamber is described.

Thermal decomposition of arsine (AsH_3) and trimethylgallium (TMG) has been analyzed by mass spectrometry. An activation energy of 35 kcal/mole is found to be associated with arsine decomposition. The possibility of GaAs growth in high vacuum from pure TMG and elemental arsenic (As_4) source is demonstrated and growth kinetics in both (TMG, As_4) and (TMG, AsH_3) systems is investigated. In particular, the growth mechanisms involved let the possibility for localized epitaxy.

1 - INTRODUCTION

MOVPE process involves several types of mechanisms both in the gas phase and at the surface.

When carried out at atmospheric pressure the growth in MOVPE appears to be only diffusion limited in the gas phase and the homogeneous or heterogeneous decomposition reactions are not the limiting step [1,2,3]. In order to investigate the heterogeneous decomposition reactions, molecular beams of metalorganic and hydride compounds are used. These experiments taking place in a high vacuum system the boundary layer above the substrate is suppressed; interactions in the gas phase are excluded and the growth is only surface controlled. The surface analytical tools available in high vacuum allow the study of the metalorganic and hydride interactions with a GaAs surface at an atomic scale. These informations are essential for the understanding of the fundamental growth mechanisms.

In a first part we describe the mass spectrometer analysis of the thermal decomposition in a furnace of the reactants. Then the interactions of the room temperature vapor species on a heated GaAs surface are studied. A second part is devoted to the growth kinetics analysis in the (As_4 , TMG) and (AsH_3 , TMG) systems. Growth characterisation being made in situ. In a last section an original property of this technique : selective epitaxy, is demonstrated.

2 - EXPERIMENTAL

The vacuum system which has been used for this study is a conventional molecular beam epitaxy apparatus. It (fig. 1) consists of a 43 cm stainless steel bell jar with a 1300 l/s oil diffusion pump

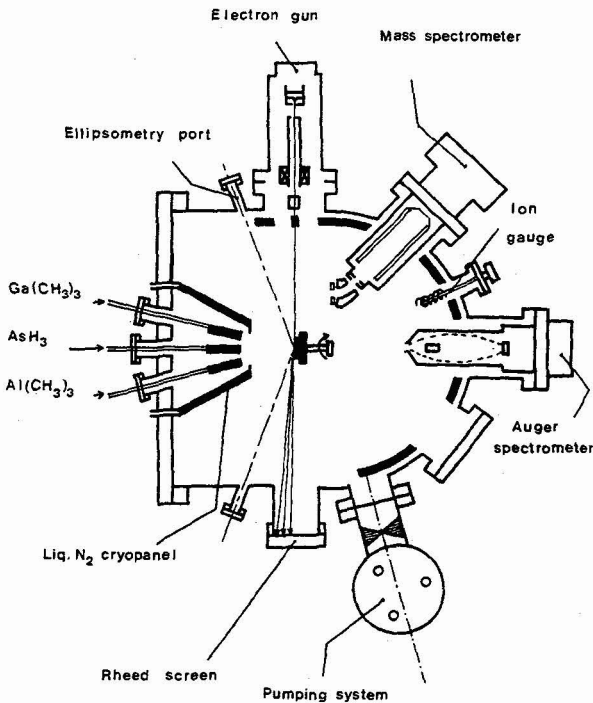


Figure 1 -
Experimental set up

fig1

connected to the work chamber via a liquid nitrogen trap, a titanium sublimation pump and cryopanel.

A quadrupole mass analyser (Riber QMM 17) is used to measure the residual background partial pressures and to analyse the decomposition products of the gases.

A RHEED system, consisting of a 25 keV electron gun which delivers a colimated beam at grazing incidence on the samples is used to observe the structural surface changes during thermal treatments and growth.

The cleanliness of the surface is assessed by an Auger spectrometer (3 keV electron gun, CMA).

A fixed wavelength ellipsometer monitors the growth in real time indicating surface roughness changes. In the case of GaAs/Ga_{1-x}Al_xAs heterojunctions it determines aluminium concentration, interface sharpness and growth rates.

The sample is introduced via an interlock chamber and is mounted on an internally heated molybdenum block. Its temperature is measured by a chromel-alumel thermocouple inserted in the sample block.

The system has been modified to accomodate arsine as well as organometallics. The vapors species are supplied from cylinders via capillary tubes and introduced through UHV leak valves and are pressure controlled. The outlet of the tubes are specially designed to diffuse the gas streams and direct them uniformly towards the substrate. At present, the system is equipped with pure arsine, TMG, and TMA gaseous sources and a conventional arsenic (As₄) cell.

3 - PRELIMINARY STUDIES

a) - Trimethylgallium-substrate interaction and thermal decomposition

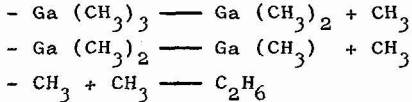
Trimethylgallium (Ga(CH₃)₃ : TMG), either pure or at a 1 to 1 dilution in H₂ is directed to a GaAs surface. As monitored by AES and RHEED, in this case GaAs surface is left unchanged. In particular in contrast with conventional MOVPE, gallium droplets are never detected.

The same behaviour is observed when exposing a Si₃N₄ or SiO₂ covered Si wafer heated at 700 °C.

The thermal decomposition in a furnace of either pure or at a 1 to 1 dilution in H₂ is analyzed by mass spectrometry. Non dissociated TMG is partially cracked in the ionization chamber of the mass analyzer in Ga(CH₃)₂, Ga(CH₃), Ga and CH₃. The thermal dissociation of TMG leads to a decrease of the Ga(CH₃)₂ and increase of Ga(CH₃), Ga and CH₃ peaks. Up to 800 °C, free gallium produced by the TMG dissociation is neither deposited on a substrate nor in the furnace.

The final products of the thermal dissociation of TMG in our conditions are believed to be mainly Ga(CH₃), CH₃ and C₂H₆.

Therefore under high vacuum conditions and low H_2 partial pressure we propose the following reactions for the decomposition of TMG which have been already established by Jacko and Price [4] in other conditions :



No free gallium.

b) - Arsine substrate interaction and thermal decomposition

It is well known that elemental arsenic (As_4 of conventional MBE cell) impinging on a GaAs substrate heated at 700 °C prevents its decomposition. In this case the bonding indium of the substrate holder reacts with the arsenic to make an InAs compound.

In contrast when arsine (AsH_3) either pure or at a 10 to 100 dilution in H_2 is used, no InAs is produced on the sample holder although the surface is stabilized by an intermediary element of the arsine decomposition. We can deduce that the heated substrate doesn't decompose arsine into arsenic.

The arsine thermal decomposition in a furnace has also been studied by mass spectrometry and compared to similar experiments by Calawa [5]. A special furnace using a pyrolitic boron nitride tube sealed on a molybdenum capillary is used (fig. 2). Tantalum radiation shields surround the furnace.

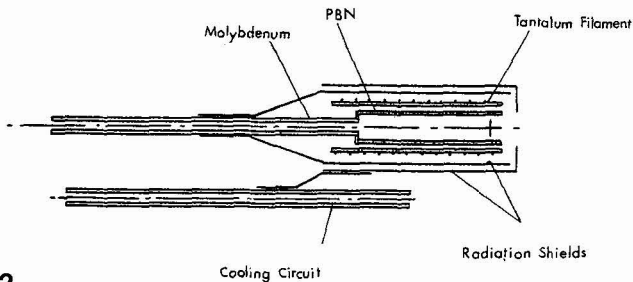


Figure 2 -
 AsH_3 furnace

fig2

The data are corrected using the cracking pattern of the arsine in the mass spectrometer. The results are given in fig. 3 for the evolution of the dissociated gases as a function of the furnace temperature.

The decomposition of arsine leads to H_2 , As, AsH, As_2 and As_4 .

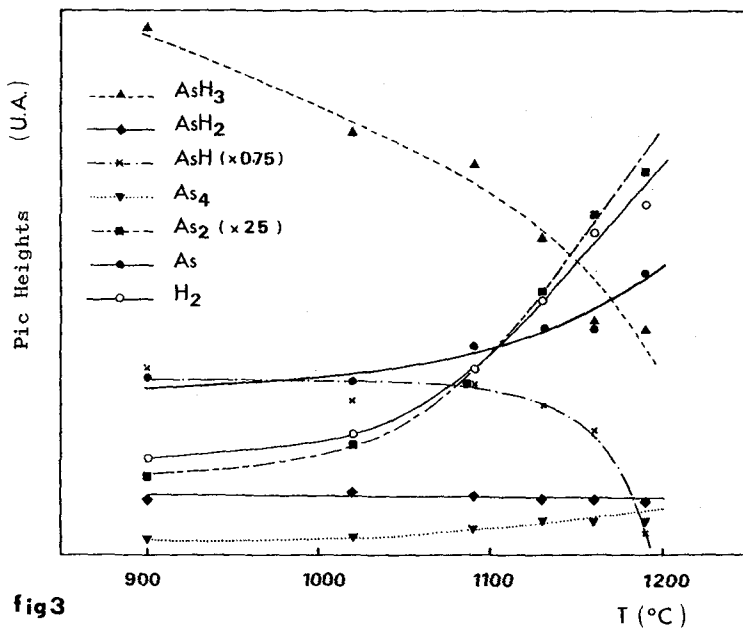
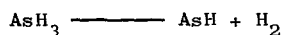


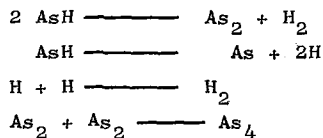
Figure 3 -
AsH₃ cracking
pattern evolution

fig3

Below 1100 °C, only a first step of the decomposition is reached :



In particular, if the data are corrected as mentioned above, the AsH₂ species are constant and produced only by the ionization chamber. The dissociation of AsH appears to be the step limiting process. It occurs only above 1100 °C in our set up, according to the following schemes :



Assuming a first order decomposition reaction with respect to arsine pressure and calibrating the quadrupole mass analyzer on AsH₃ and H₂ pressures, an activation energy is estimated to be 35 kcal/mole for the arsine decomposition and 37 kcal/mole for H₂ production.

4 - GaAs GROWTH KINETICS

a) - Growth from pure TMG and As₄

The substrate used are Czochralsky semi-insulating (Cr doped) GaAs (001) oriented wafers. Chemical treatment before the introduction

of the sample follows this procedure :

Trichlorethylene and acetone degreasing, $H_2SO_4 : H_2O : H_2O_2$ (20.1.1) etching, desionized water rinsing.

Prior to growth a heat treatment of the sample is used in order to decompose the gallium and arsenic oxides.

Fig. 4 shows the growth rate dependence on the TMG partial pressure (at the sample), for given As_4 flow and substrate temperature.

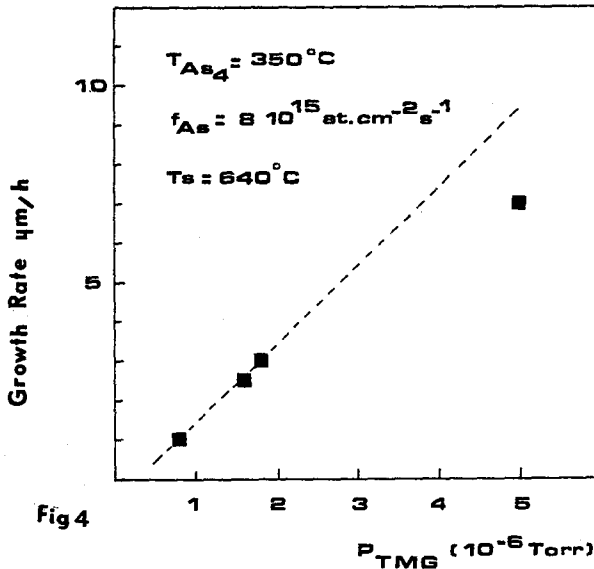


Figure 4 - Growth rate versus TMG partial pressure

For a flux ratio $f_{As_4}/f_{TMG} \gg 1$, growth rate is proportional to TMG flow. Higher TMG pressures leads to non linear dependence. This can be due either to a control of the growth rate by the As_4 flow, or more probably to an inhibition of the growth due to a high coverage of the surface by undecomposed gallium compounds or methyl and ethyl adsorbed species.

The temperature dependence of the growth rate for a given As_4 and TMG partial pressure is shown in fig. 5. The activation energy associated with the temperature dependence of the growth rate between 600 °C and 700 °C is 0,6 kcal/mole.

This means that in this temperature range TMG decomposition does not limit the process and growth rate is proportional to the impinging flux as in classical MBE [6].

Below 600 °C the growth rate decreases with an apparent activation energy of 42 kcal/mole. The growth process is then limited by a step of the TMG decomposition.

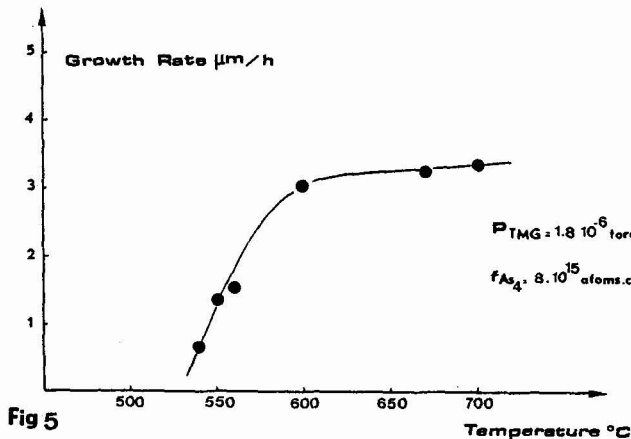


Figure 5 - Temperature dependence of the growth rate from TMG and AsH₃

b) - GaAs growth from TMG and AsH₃

The growth of GaAs from room temperature TMG and AsH₃ in vacuum has been already reported [7]. However in our experimental set up, under the same temperature and TMG flow conditions, if room temperature flow of arsine either pure or at a 10 to 100 dilution in H₂ is substituted to arsenic, no growth is observed. A higher arsine partial pressure on the sample, for the same total chamber pressure can explain the experimental differences with the work mentioned above. To bring active arsenic species (As, As₂, As₄) at the surface, the furnace described (fig. 2) has been used to crack AsH₃. Fig. 6 shows the mass spectrum during growth. It appears

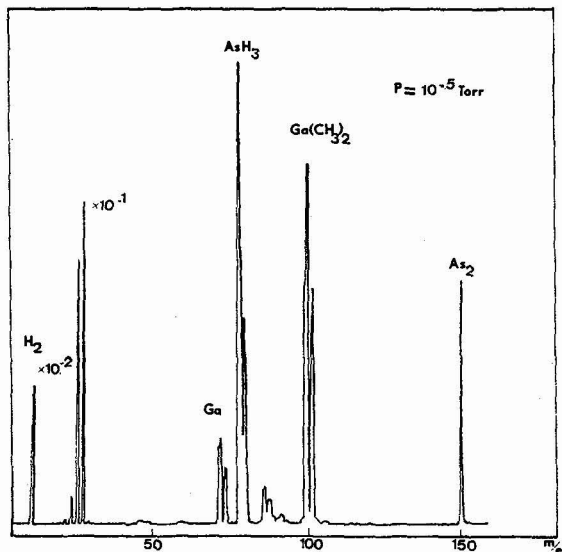


Figure 6 - Mass spectrum during growth from Ga(CH₃)₃ and AsH₃

fig 6

that for the same TMG flow, the growth rate is lower in this case compared to that obtained with As_4 (fig. 7).

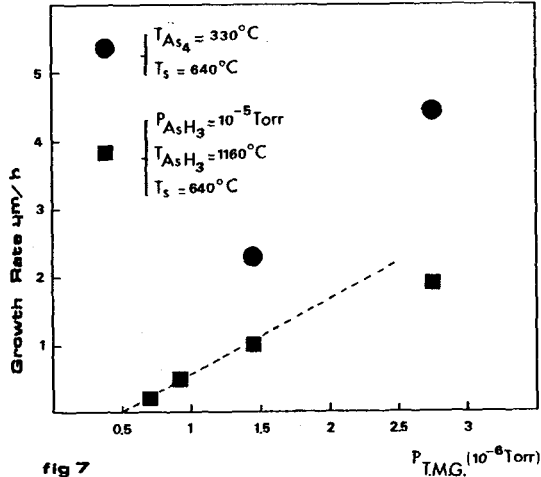


Figure 7

The poisoning of GaAs surface by the hydrogenated arsenic products probably AsH may explain this behaviour as well as the observed non decomposition of arsine by the heated substrate. For high TMG flow the same inhibition of the growth rate is observed.

The influence of the temperature on the growth rate has also been studied. It appears that no variation is observed between 600 °C and 700 °C while below 600 °C growth rate decreases. Complementary studies are needed to evaluate the activation energy corresponding to the slope of the curve.

To summarize we propose the following simple scheme for GaAs. Growth under high vacuum in (TMG + As_4) or (TMG + cracked AsH_3) systems.

- There is no free gallium in the gas phase and on the surface when arsenic species are absent.

- Arsine is not decomposed on a heated (500 to 700 °C) surface but prevents the GaAs decomposition.

- Arsenic species can only be chemisorbed on the surface when gallium dangling bonds are present, as in MBE [8].

- Once the arsenic species are chemisorbed, gallium containing organic molecules can be chemisorbed and they can form a complex with arsenic.

- The methyl radicals present in such a complex are then freed and a GaAs molecule is incorporated.

- The exact role of hydrogen is not clear at present time.

5 - ELECTRICAL PROPERTIES

Layers grown with As_4 are mirror like and uniform (within 5 %) in thickness on a 6 cm^2 surface. The residual doping level is P type at about 10^{19} at/cm^3 . No carbon is detected in these layers by Auger spectroscopy.

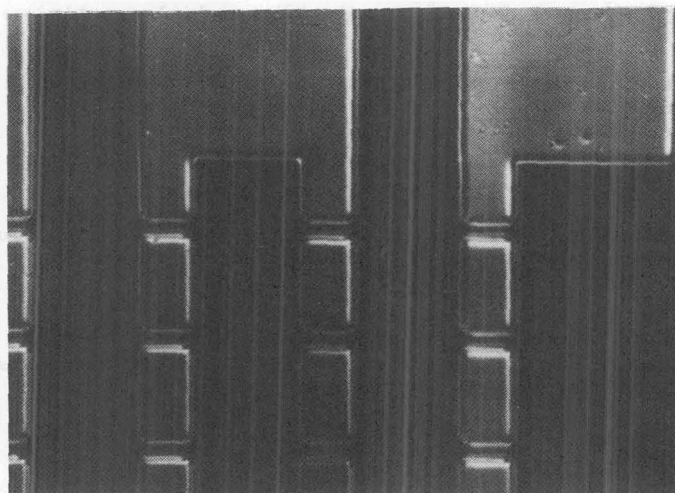
When arsine is substituted to As_4 , the layers remain p type but the doping level decreases to 10^{16} with a mobility of 300 and $1400 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature and 77 K respectively.

Complementary studies are needed to determine which elements are responsible for this doping level.

It appears from first SIMS analysis that the carbon concentration in the layers is comparable with the one in the substrate. Carbon contribution to the high doping level can thus be ruled out.

6 - A SPECIAL FEATURE : LOCALIZED EPITAXY

Taking advantage of the surface catalyzed growth process, particular growth conditions have been found which lead to selective epitaxy. As already noted, growth occurs only when Ga dangling bonds are present at the surface. By using a Si_3N_4 or SiO_2 covered GaAs, and opening windows in the dielectric top layer, metal organic MBE growth takes place only in the windows as shown in Fig. 8.



It appears from Fig. 8 and the SEM cross section examination of the layers that the growth edges are well defined and smooth.

It is important to notice again that no deposition occurs on the dielectric film. This is in contrast with MBE or MOVPE technique [9] where

polycrystalline GaAs films develop on these masked regions, leaving the technological problem of their subsequent removal.

7 - CONCLUSION

From metal organic and hydride thermal decomposition studies it appears that under our experimental conditions TMG does not lead to pure gallium production.

A TMG beam impinging on a heated gallium arsenide substrate does not change its surface composition, furthermore gallium droplets are not observed.

The possibility of epitaxial growth of GaAs from pure TMG and As_4 has been established. The layers are mirror like and their thickness uniformity is better than 5 % over a 6 cm^2 surface. The residual doping level is lowered when using arsine but remains p type at present.

However if the doping level can still be lowered this process may become very attractive : particularly the large choice of metalorganic compounds available permits the extension of this process to the growth of a large class of semi-conductor alloys. The vapor species being considered as quasi infinite sources, the molecular beam intensity will be reproducible and easy to control. When designing a system for ternary or quaternary material growth, gas mixing is possible, at least of elements within the same groups (III or V). Therefore the problem of composition uniformity, which is a limitation in MBE, might be partly solved.

The growth being possible only on arsenic stabilized surfaces experimental conditions have been found where selective epitaxy takes place. This special feature may present technological advantages.

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