MULTICHAMBER REACTORS : A SOLUTION TO THE PROBLEM OF GRADED
HETEROINTERFACES IN HOT-WALL VPE SYSTEMS

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Résumé. - La production de couches homoépitaxiales de bonne qualité par la méthode de croissance dite "des hydrures" est une technique bien connue en ce qui concerne les binaires III-V les plus répandus. Cependant, il est difficile d'obtenir des hétérointerfaces abruptes entre par exemple Ga In As et In P, l'écoulement du flux gazeux étant généralement lent afin de suivre le profil de température voulu entre sources et substrat. Dans des conditions d'utilisation normales, un changement de composition correspondrait à un temps équivalent à la croissance de plusieurs milliers d'Angströms de matériau.

Ce papier décrit l'obtention d'hétérojonctions abruptes obtenues dans un nouveau type de réacteur, comprenant quatre chambres de croissance indépendantes, où peuvent être établies des conditions de flux gazeux en état stationnaire et les changements de composition sont obtenus en déplaçant rapidement l'échantillon d'une chambre à l'autre. Il a été possible, avec ce réacteur, d'obtenir des largeurs d'interfaces de l'ordre de 150 Å.

Abstract. - The "hydride" growth process is well established as a technique for producing high quality homoepitaxial layers of the common III-V binary materials. However, it is difficult to obtain abrupt heterointerfaces for example between Ga In As and In P, as the gas speed is generally slow in order for the gas to follow the desired temperature profile in its passage through the source to substrate. Thus under normal conditions, a change of composition will occur in a time corresponding to the growth of several thousands of angströms of material.

This paper describes the growth of abrupt heterojunctions which have been achieved in a new geometry reactor, based on four separate growth chambers. In each chamber, the gas flow conditions for the growth of a specific composition are stabilised and changes of composition are achieved by rapidly moving the sample from one chamber to another. This new reactor has allowed us to grow multiple heterojunctions with an interface abruptness of better than 150 Å.

1. **Introduction.** - The "hydride" vapor phase epitaxy of (Ga, In) (As, P) alloys is a well-known method (1-5), which consists of a hot-wall reactor working at atmospheric pressure. The gaseous species are synthesized in a high-temperature region by reacting hydrogen chloride with liquid Indium and Gallium sources, and pyrolysing Arsine and Phosphine downstream. Then the gas flow is cooled by a negative temperature gradient which is imposed between the sources and the substrate. This cooling of the gaseous phase results in growth onto the substrate.

The use of heterostructures for the fabrication of devices requires lattice matching on the substrate, and very sharp interfaces between different layers. As the gas flow has to follow the desired temperature profile, the gas velocities are usually very low and the compositional change of the gas phase becomes very slow. An alternative to overcome this problem is to use

multichamber reactors (5-7), where the substrates are moved between different steady state gas phase compositions.

2. Principle of conventional hydride-VPE growth of III-V alloys and kinetic limitations

A sketch of a conventional reactor is given in fig. 1.

Fig. 1: Conventional Hydride VPE reactor

This reactor usually consists in a fused silica tube heated by a multi-zone furnace which impose a negative temperature gradient between two regions.

a/ In the source region (750-900°C), all the gaseous group III species necessary for the growth are formed by reacting Hydrogen chloride HCl diluted in Hydrogen with liquid Indium and Gallium. These metallic sources are usually separated in two different boats, but In-Ga melts have been used (8-9).

Arsine (AsH_3) and Phosphine (PH_3) are introduced downstream and are pyrolysed in Arsenic and Phosphorus vapours.

The synthesis of GaCl , InCl , P_{vap} , As_{vap} can be described by the following set of chemical reactions :

The resulting gas phase is assumed to be in thermodynamic equilibrium (9-13). The proximity of thermodynamic equilibrium is almost obtained for the group V compounds, as reactions 3 and 4 are homogeneous decompositions in the gas phase (first order reactions). This condition is quite difficult to achieve for reactions 1 and 2. The quasi-equilibrium is obtained in a narrow partial pressure range which depends on :

- source geometry
- total gas flow rate
- reactor design
- kinetics of reactions 1 and 2

As reactions 1 and 2 are heterogeneous reactions between a gas and a liquid, kinetics are greatly influenced by the geometry.

In order to obtain a good reproducibility, it is better to be in quasi-equilibrium conditions and therefore, to use

- large liquid/gas contact areas.
- boat shapes which increase the contact duration between gaseous products and liquids.
- relatively low flow velocities.

Figure 2-a shows that the growth rate of In P is significantly changed by the design of the boats which contain the In source.

b/ Assuming that the previously described conditions are carried out, the gas phase is swept downstream in a temperature gradient ($\sim 10^\circ\text{C}/\text{cm}$), in order to obtain a metastable equilibrium. This cooling of the nutrients results in growth onto the substrate, which can be described by :

All the pseudo-binary system $\text{Ga}_x \text{In}_{1-x} \text{As}_y \text{P}_{1-y}$ can be covered with an appropriate ratio between (5) and (5').

In VPE reactors, these reactions occur far from equilibrium and the growth is significantly influenced by kinetics and parasitic effects (14), as :

- substrate orientation.
- nucleation on the walls of the reactor.
- mass transport (convective or diffusive flows).

The parasitic nucleation on the walls can be minimized, using an excess of HCl, but mass transfer is clearly responsible for reproducibility, even in the case of homoepitaxy (figure 2-b). The flows must be carefully adjusted a long time before growth, in order to increase the reproducibility.

Fig. 2

3. Hetero interfaces obtained in conventional and multichamber reactors

a/ Figure 3 shows the three important mechanisms involved in CVD growth processes, i.e. :

- mass transport.
- heterogeneous chemical reactions, where liquid/gas and solid/gas interfaces are involved.
- homogeneous chemical reactions, taking place in the gas phase.

Fig. 3: V.P.E. mechanisms

Homogeneous reactions are usually well described by thermodynamic analysis, because they take place in the gaseous phase, where the reaction kinetics are rapid, and the system is well defined when the free energy function $G(T, P, n_i)$ is a minimum. The definition of a system by minimisation of its free energy gives a set of n_i values which are only dependant upon the pressure, the temperature and the composition of the nutrient phase, or the initial composition of the system before reactions occur.

Heterogeneous growth reactions are involved in mass transfer and chemical reactions which take place at surface sites. These chemical reactions only depend on the concentration of the reacting species in the nutrient phase, on the coverage ratio of the active surface, and on adsorption and desorption energies ; kinetics are usually more rapid than mass transfer during composition changes ; otherwise, they are time-independent, and have been studied by statistical physics and the theory of rate processes (15-17).

b/ The only time dependent parameter in crystal growth is mass transport, assuming that heat transfers are in steady-state (18-19). In a multicomponent non isothermal fluid, mass, momentum and energy are conservative, and the continuity equation, which takes into account the convective and diffusive fluxes, expresses the local gain of mass density for each species i , due to convection v and diffusion j_i :

$$\frac{\partial \rho_i}{\partial t} = - \text{div} \left[\rho_i \vec{v} + \vec{j}_i \right]$$

The diffusive flux j_i is a combination of two terms : concentration gradient-induced diffusion and thermal diffusion :

$$\vec{j}_i = - \frac{C^2 M_i M_M}{\rho} D_{i,M} \left[\text{grad} (X_i) + k_T \text{grad} (\ln T) \right]$$

where : M_i is the molar mass of i

M_M is the molar mass of the main gas

$D_{i,M}$ is the mutual diffusion coefficient of i and M

X_i is the molar fraction of i

K_T is the thermal diffusion coefficient

ρ, ρ_i are the average and i -th species mass density

This differential equation can be computed and gives the spatial and time-dependent concentration of each species.

Figure 4 shows the response of the gas phase composition in the reactor (assumed to be cylindrical), without taking into account the chemical reactions and temperature gradient, when a new gas is introduced in the reactor at the time t_0 .

Fig. 4: Diffusion
in the gas phase

This simplified example gives an idea of the influence of transient mass transfer and clearly demonstrates the difficulty of growing binary or quaternary material directly on In P, as a steady state after gas switching is not reached within a few minutes.

A solution to overcome this problem is to use a "waiting chamber", where the sample is covered and/or protected by the appropriate amount of arsine and phosphine until the steady state is reached.

An alternative is to use a multichamber reactor (figure 5), which allows the growth of a complete double heterostructure in a single run.

Fig. 5: Four chamber-reactor

a- Organisation

b- Double heterostructure growth sequence

This reactor is composed of four parallel and independent VPE reactors ("chambers") where all the facilities for gas supplying and monitoring are set up. Each chamber contains two separate In and Ga boats, except for the etching chamber, where the substrate surface is etched before growth. Therefore, it is possible to adjust in each chamber the appropriate gas phase composition in order to grow any solid $\text{Ga}_x \text{In}_{1-x} \text{As}_y \text{P}_{1-y}$ material, and to be in steady state before any growth.

These four chambers are linked downstream by a fifth common tube, in order to transfer the sample from one chamber to another. This is achieved by using an automatic transfer mechanism, which makes the movement possible within two seconds (figure 6).

Fig. 6

During these two seconds, assuming that a deposit occurs during the passage in the common tube with the usual growth rate, the perturbed interface should have a thickness of $\sim 100 - 150 \text{ \AA}$.

In order to characterize these heterointerfaces, bevels are chemically etched, using a Br_2 - methanol solution (20,21). Using this technique, it is possible to observe the evolution of defects in each layer and at the heterointerfaces. The composition of the different layers which have been revealed on the bevel is analysed by scanning Auger spectroscopy, as shown in figure 7.

Fig. 7: Auger spectroscopy on a bevelled sample

The results obtained are in good agreement with the assumption of a continuous deposit during the transfer of the sample. Figure 8-a shows the heterointerface abruptness obtained on a In P/Ga In As heterostructure grown in this reactor using a transfer duration of 5 seconds, by analysing the Arsenic concentration on a bevel angle of 0.17° . The interface abruptness is $190 \text{ \AA}$, but it can be seen that the signal transition is composed of three parts with different slopes, and the real thickness might be less than $150 \text{ \AA}$. Figure 8-b represents the Phosphorus analysis of a double heterostructure for laser application. The two interfaces are less than $100 \text{ \AA}$.

Fig. 8: Auger measurements

In order to test the properties of these double heterostructures, broad area lasers have been fabricated (22) ; the current densities of 2 KA/cm^2 which have been measured demonstrate that the properties of these interfaces are quite good.

4. Conclusion - The purpose of this study was to demonstrate that changes of the gas composition for growing heterostructures cause non-steady state mass transfer in a VPE-reactor, and that this is not convenient for growing double heterostructures, as the sample has to be protected until steady states conditions are obtained. It has been shown that the use of a four chamber reactor was a good alternative to obtain sharp interfaces without degrading the properties of the materials. The interfaces sharpness obtained are about $100 \sim 150 \text{ Å}$, and by using lower growth rates, can be probably reduced.

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