ZnO GROWTH BY MOCVD: NUMERICAL STUDY

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Abstract

In order to analyse the growth of ZnO by MOCVD, a numerical model has been developed to simulate the gas flow in a horizontal reactor. A two–inlet system, one inlet for the Zn precursor and the other one for the oxygen precursor, has been analysed in the framework of the numerical simulation. This model takes into account the momentum conservation equation coupled with the heat transfer and mass transport of chemical species. Different Zn precursors (DEZn, DMZn and DMZn–TEA) and oxygen precursors (*tert*–butanol, *iso*–propanol and acetone) as well as carrier gases (H_2 and N_2) are considered. The effects of simulated experimental conditions on the fluid dynamics inside the reactor and, consequently, on the growth rate of ZnO layers have been analysed.

1.– Introduction

ZnO has attracted much attention in the last years. Its wide bandgap, 3.37 eV at room temperature, and its large exciton binding energy (60 meV) makes it a promising material for optoelectronic devices working in the blue and ultraviolet region, such as light–emitting devices and laser diodes [1]. Nowadays MOCVD is an industrially important technique for manufacturing layers to be used in optoelectronic devices [2]. Nevertheless, several problems remain in the MOCVD technique, including the need for expensive reactants and the large number of parameters that must be precisely controlled to obtain the necessary uniformity and reproducibility. The MOCVD process is critically dependent on the fluid dynamics of the reacting and carrier gases. Quantitative and qualitative understanding of fluid dynamics associated with a particular reactor design is central to achieve improvements in efficiency, crystal production and growth uniformity.

In the growth of ZnO by MOCVD, the most frequently used oxygen precursors have been O_2, H_2O, N_2O, acetone and alcohols (*tert*–butanol, *iso*–propanol and acetone). O_2 and H_2O can react violently with common Zn precursors (DEZn, DMZn and DMZn–TEA), while alcohols, which experimentally show good results, and acetone are less reactive. Nevertheless, it is still desirable that the mixture of the Zn and Oxygen precursors occurs as near as possible to the substrates, in order to avoid possible pre–reactions. A two–inlet design can be used to avoid premature reactions and permit a better control of partial pressures.

In this work, hydrodynamic differences between a two–inlet and a single–inlet configuration and their effects on the growth are analysed. In addition, the influence of the carrier gas (H_2 or N_2) on the "two inlet" system is studied within the same framework. Finally we examine the variations in uniformity of the growth rate along the susceptor due to differences in the precursors diffusion coefficients.

2.– System description and numerical simulation

The simulated system consists of a horizontal tapered silica reactor located in an MOCVD equipment (Quantax 226 refurbished by EMF Ltd). The longitudinal section and a 3–D scheme are shown in fig.1. The system is well adapted to the growth using two gas inlets, the lower one for the oxygen precursor (*tert*–butanol, *iso*–propanol or acetone) and the upper one for the Zn precursor (DEZn, DMZn or DMZn–TEA).

Inside the reactor, two 2" substrates can be placed on a static graphite susceptor, which is heated by a radio–frequency system that allows the necessary temperature for the pyrolysis of the precursors to be attained.
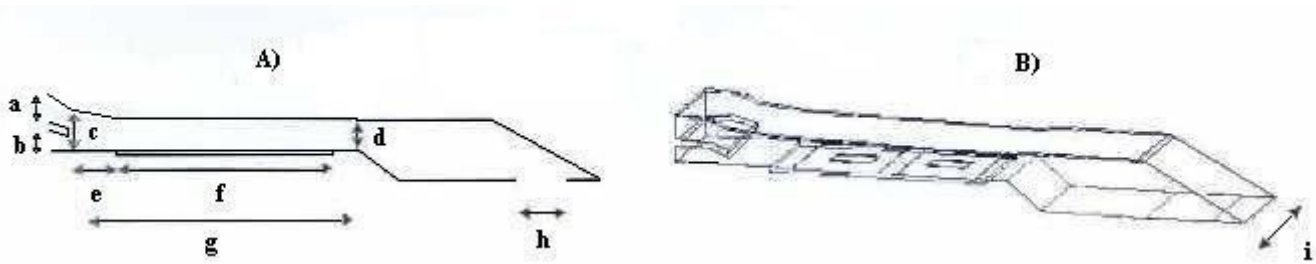
Fig. 1. Scheme of the two–inlet reactor cell.   **A)** Longitudinal section. **B)** 3–D scheme. a = upper inlet (15 mm), b = lower inlet (9 mm), c = 19 mm, d =15 mm, e = 38 mm, f = substrates wafers (120 mm), g = susceptor (150 mm), h = outlet (25 mm) and i = width of the reactor cell (66 mm).

An initial hydrodynamic characterisation of the flows in the reactor has been achieved by means of the Reynolds and Rayleigh dimensionless numbers in order to simplify the governing equations. From this analysis we can conclude that the flow is laminar in all the analysed cases (H_2 and N_2 being used as carrier gases). As a consequence, we can apply the simplifications associated with laminar flow (see below). However in the case of N_2, the Rayleigh number predicts the existence of longitudinal rolls due to the free convection in the reactor and thus, a 3–D numerical model must be used to study the distribution of these rolls and their effects on the growth rate of the ZnO layers; while in the case of hydrogen, a 2D approach is justified because the width to height ratio is large (in the order of 4) and the sidewalls have no significant influence on the flow field .

With respect to the processes inside the reactor, we can say that there are two main consecutive ones: the arrival of molecules (the Zn and Oxygen precursors) at the proximity of the substrate and the chain of reactions present in this zone (pyrolisis of the precursors and surface reactions). The first process is controlled by the velocity field of the fluid inside the reactor and by the diffusion of the precursor species due to their concentration gradients. The second one is controlled by the rate of the reactions that take place during the growth process.

The effect of consecutive processes is that the growth rate is limited by the slowest one. From experimental results [3,4], we can conclude that when the substrate temperatures are in the range of 325–400ºC the growth takes place in a mass transport regime. Then, we can assume a fast chain of reactions and focus on the hydrodynamic behaviour and its influence on the growth process.

The numerical calculations of fluid flow, temperature and concentration fields, have been made using a computational fluid dynamics code FLUENT [5]. In this code the individual identity of the conservation equations is based on a finite difference/control volume technique. The relevant governing equations are:

   – Continuity equation:

$$\vec{\nabla}\left(\rho\,\vec{v}\right)=0 \tag{1}$$

   – Momentum conservation equation:

$$\vec{\nabla}\left(\rho\,\vec{v}\,\vec{v}\right)+\vec{\nabla}p+\vec{\nabla}\overleftrightarrow{\tau}=\rho\,\vec{g} \tag{2}$$

   – Species conservation equations:

$$\vec{\nabla}\left(\rho\,\vec{v}\,m_i\right)=\vec{\nabla}\,\vec{J}_{i,j} \tag{3}$$

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– Energy conservation equation:

$$\vec{\nabla}\left(\rho\widehat{H}\,\vec{v}\right) + \vec{\nabla}\,\vec{q} + p\left(\vec{\nabla}\,\vec{v}\right) + \vec{\nabla}\left(\widehat{H}\,\vec{J}_{i,j}\right) + \overleftrightarrow{\tau}:\vec{\nabla}\,\vec{v} = -S_h \qquad (4)$$

In these equations, ρ is the fluid density, $\vec{v}$ the fluid velocity, p the static pressure, $\vec{g}$ the gravity vector, $\overleftrightarrow{\tau}$ the conventional stress tensor, m_i the mass fraction of species i, $\vec{J}_{i,j}$ the diffusion flux of species i in the carrier j ($\vec{J}_{i,j} = -\rho D_{i,m}\vec{\nabla}m_i$), $D_{i,m}$ the mass diffusion coefficient of species i, $\widehat{H}$ the enthalpy per unit mass, $\vec{q}$ the energy flux relative to mass average velocity and S_h a source term which includes the sources of enthalpy due to chemical reactions.

This set of algebraic equations is solved by a semi–implicit iterative scheme which, after performing a number of iterations, converges towards the correct solution within a residual error. The calculations are continued until the error has decreased to a required value.

We have used two computational domains. A 2–D domain of 2624 (82 x 32) cells adapted to the geometry of fig.1A, and a 3–D domain of 19806 (43 x 33 x 14) cells adapted to the geometry of fig.1B. In order to avoid divergence problems and mathematical difficulties which are related to local variations of flow values, the density of cells in the grid has been taken to be non uniform. This density is higher near the susceptor (where the gradient of species concentration is strong) and between the inlets and the susceptor (where the mixture of fluids with different characteristics is present). We have tested the results with a double cell density and similar results have been obtained, justifying the validity of the chosen grid.

3.– Numerical results

We have studied the ZnO growth in a two–inlet MOCVD system under usual experimental conditions [3] (total flow = 5.5 slm, substrate temperature = 380ºC, total pressure = 1 atm, partial pressure of Zn precursor (P_{Znprec}) at the upper inlet=1.39×10^{-4} atm and partial pressure of oxygen precursor ($P_{Oxygenprec}$) at the lower inlet=6.93×10^{-4} atm).

In order to study the "two–inlet effect" [6] and its ability for avoiding pre–reactions between the Zn and oxygen precursors, we have analysed the mole fraction of Zn precursor in the lower part of the reactor (at the beginning of it) as a function of the ratio (R) between the upper inlet flow and the lower inlet flow.

In the case of DEZn and *tert*–butanol being used as precursors, and H_2 as carrier gas, the results are summarized in fig. 2. Due to the effect of the lower inlet flow, for R values lower than 2.5 the mole fraction of DEZn is very low in the zone prior to the substrate wafers. Thus, the complete mixture of DEZn and *tert*–butanol occurs over the substrate and the possible pre–reactions between them can be avoided. A similar effect occurs with other Zn precursors (DMZn and DMZn–TEA) also studied in this work, because the main responsible fact of the "two–inlet effect" seems to be the forced convection, the partial pressure of the precursor being irrelevant (~10^{-4} atm) on the flow properties.

Another relevant aspect is the influence of the Zn precursor difussion coefficient on the uniformity of the growth rate along the reactor. The results for DEZn, DMZn and DMZn–TEA, when *tert*–butanol is used as oxygen

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precursor (VI/II ratio = 5) and H_2 as carrier gas, are shown in fig.3. The best uniformity is obtained when DMZn–TEA is used. This fact is mainly due to its lowest diffusion coefficient ($D_{DMZn,H2} > D_{DEZn,H2} > D_{DMZn-TEA,H2}$). In this effect, the diffusion coefficient of the oxygen precursor (*tert*–butanol, *iso*–propanol or acetone) is not relevant because the VI/II ratio is sufficiently high.
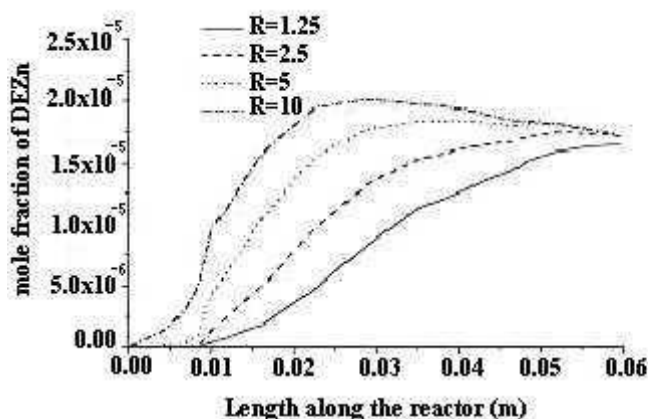

Fig. 2. Mole fraction of DEZn as a function of the length along the reactor for different values of R (ratio between the upper inlet flow and the lower inlet flow)
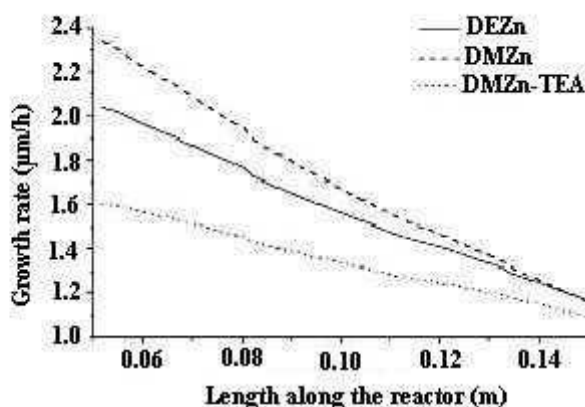
Fig. 3. Growth rate as a function of the length along the reactor for different Zn precursors

When N_2 is used as carrier gas similar effects have been observed. Nevertheless some new phenomena, as the presence of longitudinal rolls, appear.

4.– Conclusions

When the precursors are introduced in the reactor through different inlets, the hydrodynamic conditions on the first part of the reactor are extremely sensitive to the boundary conditions on the inlets. This fact can be used to avoid undesired pre–reactions between the Zn and oxygen precursors. On the other hand, we can conclude that the uniformity of the growth rate along the reactor increases when the diffusion coefficient of the limiting rate growth precursor decreases.

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