

## THE RESEARCH OF ZNO - MOCVD OPERATING ENVIRONMENT AND EXPERIMENTAL VERIFICATION

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### ABSTRACT

Currently, metal organic chemical vapor deposition (MOCVD) is the most suitable technology for large-scale preparation of thin-film materials, with the advantage of large epitaxial area, good repeatability, precise componential control, deposition rate, etc. It is a multi-disciplinary complex system, and MOCVD process contains a large number of complex physical and chemical processes with complicated reaction mechanism and growth kinetics. The core part of MOCVD system is reactor. In order to grow high-quality thin-film by MOCVD, the flow fields, thermal fields and chemical reactions mechanism of MOCVD reactor must be studied in depth. In this paper, MOCVD was 3D numerically simulated by computational fluid dynamics software. The flow field, the thermal field and the gas-phase pre-reaction that affect the structure and properties of thin-films have been intensively studied, and the experimental results and the simulation results under same operating condition are compared to verify the reliability of the simulation results. Achievements are as follows: 1. Use home-made MOCVD equipment to grow thin-films which can be used to machine semiconductor LED chip on polished silicon substrate and collect parameters in the process as boundary conditions of numerical simulation. The N & K versatile film tester is also used to measure the thickness of the sample and to analysis the thickness distribution trends of thin film on a substrate, preparing to verify the reliability of the simulation results. 2. Establish the geometric model and grid model of MOCVD reactor chamber, and import to computational fluid dynamics software Fluent for numerical simulation, and then compare the results of numerical simulation and experimental results. It is found that the simulation deposition rate distribution curve after fitting with an empirical formula generally coincides with the experimental distribution curve. 3. Analyze the distribution of temperature, velocity, mass fraction, deposition rate and the pre-reaction conditions which seriously affect the quality of films, and get to know the state of thermal and flow fields in the reaction chamber and the conditions and regions of pre-reactions. Due to the low gas velocity in the area near the center of the substrate, it more greatly subjects to DEZn

and O<sub>2</sub> reaction and decomposition reaction of DEZn, which also explains the film's thinner deposition on the inner circumference of the substrate, namely, consumption of raw materials being not promptly replenished.

### 1. INTRODUCTION

ZnO is an II-VI group of wide bandgap compound semiconductor materials, possessing large exciton binding energy. It is rationally expected to be applied to the field of ultraviolet detectors, optoelectronic devices, transparent thin-film transistors, surface acoustic wave devices, sensors, etc [1-3]. In the recent decade, rapid progress has been made in the above field based on ZnO. It has important research value and broad industrial prospects. The preparation of high-quality ZnO material has attracted more and more attention.

Currently, the main epitaxial growth of thin film based on ZnO is metalorganic chemical vapor deposition(MOCVD), with the advantages of large epitaxial area, strong repeatability, precise componential control and the high deposition rate, which is one of very important technical means of producing ZnO material and devices on the large scale.

MOCVD process contains a large number of complex physical and chemical processes with complicated reaction mechanism and growth kinetics [4]. In order to grow high-quality ZnO thin-film by MOCVD, the flow fields, thermal fields and chemical reactions mechanism of MOCVD reactor must be studied in depth. So it is essential to use CFD in the large-scale computation by the help of computer to solve this complex problem.

### 2. NOMENCLATURE

$\vec{v}$	[m/s]	Components of the velocity vector
$\rho$	[Kg/m <sup>3</sup> ]	Density
$t$	[s]	Time
$P$	[pa]	Pressure
$u$	[m/s]	Components of the velocity vector in the x direction
$v$	[m/s]	Components of the velocity vector in the y direction

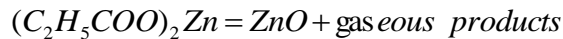
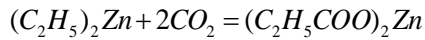
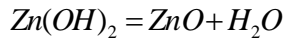
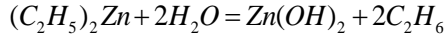
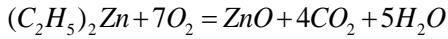
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$w$	[m/s]	Components of the velocity vector in the z direction
$S_u$	[pa/m]	Pressure source term in the x direction
$S_v$	[pa/m]	Pressure source term in the y direction
$S_w$	[pa/m]	Pressure source term in the z direction
$x$	[m]	Cartesian axis direction
$y$	[m]	Cartesian axis direction
$z$	[m]	Cartesian axis direction
$T$	[K]	Temperature
$K$	[W/(m·K)]	Thermal conductivity
$C_p$	[J/(Kg·K)]	Specific heat capacity
$S_r$	[J/(m <sup>3</sup> ·s)]	Heat source term

### 3.THEORETICAL FOUNDATION

#### 3.1 ZO CHEMICAL REACTION MECHANISMS

It has been reported that ZnO chemical reaction mechanisms with vapor sources of diethylzinc ( $Zn(C_2H_5)_2$ ; DEZn) and  $O_2$  by MOCVD in available literature [5].



#### 3.2 SIMULATION CONTROL EQUATIONS

The fluid flow problem is defined by the laws of conservation of mass, momentum, and energy. These laws are expressed in terms of partial differential equations which are discretized with a finite element based technique.

##### 1.Continuity Equation

From the law of conservation of mass law comes the continuity equation:

$$\text{div}(\rho \vec{v}) = 0 \quad (1)$$

##### 2. Momentum Equation

$$\text{div}(\rho u \vec{v}) = \text{div}(\mu \text{grad} u) - \frac{\partial p}{\partial x} + S_u \quad (2)$$

$$\text{div}(\rho v \vec{v}) = \text{div}(\mu \text{grad} v) - \frac{\partial p}{\partial y} + S_v \quad (3)$$

$$\text{div}(\rho w \vec{v}) = \text{div}(\mu \text{grad} w) - \frac{\partial p}{\partial z} + S_w \quad (4)$$

##### 3.Energy Equation

$$\text{div}(\rho v T) = \text{div}\left(\frac{k}{c_p} \text{grad} T\right) + \frac{S_T}{c_p} \quad (5)$$

##### 4.State Equation

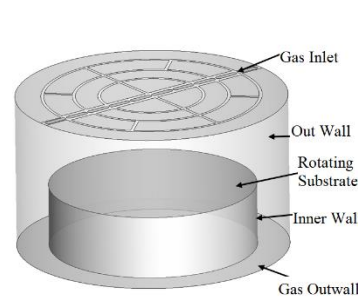
The detail form of the state equation is determined by specific situation:

$$\rho = f(p, T) \quad (6)$$

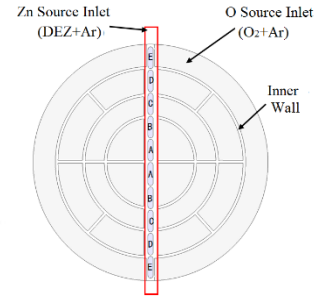
## 4.THE NUMERICAL SIMULATION OF ZNO-MOCVD REACTOR AND EXPERIMENT VERIFICATION

### 4.1 THE GEOMETRY AND GRID OF THE MOCVDREACTOR

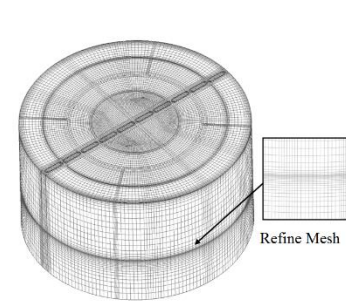
The basic structure of our modeling planetary MOCVD reactor is shown in **Figure 1**. The reactor consists of gas inlets, gas outlets, outer wall, inner wall, rotating substrate. As shown in **Figure 2**, the top of the reactor is divided into different zones. Oval holes in deep color in the figure are the inlets of zinc source, which mental-organic source and Ar gas flow into. Each pair of center-symmetrical holes for a group, together 5 groups, can be set at different flow rates. The zones in light color are inlets of oxygen source, named O Source Inlet, which oxygen and Ar gases flow into. The zones in white separate gas inlets of zinc source and the wall of oxygen source inlets. The grid of geometry reactor models are shown in **Figure 3** and **Figure 4**. After a sensitivity analysis on the mesh verified, hexahedral meshes are adopted to reconstruct this MOCVD model. Through multiple meshes test, the meshes are independent with results.



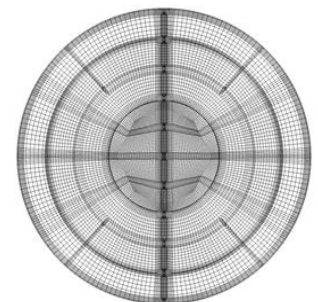
**Figure 1** Geometric model of reactor



**Figure 2** Inlets of reactor



**Figure 3** Mesh of reactor



**Figure 4** Mesh of inlet Face

### 4.2 BOUNDARY CONDITION

On the basis of flows features in MOCVD reactor, assumptions are made:

- the gases mixture behaves as a continuum under steady state conditions.
- The system conform to laminar condition [6-8].
- The graphite susceptor temperature 734K, outer wall temperature 573K and inlet wall temperature are uniform.
- Other walls of the reactor conform to insulated boundary condition.

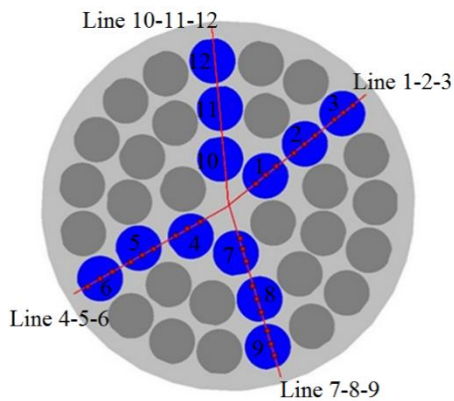
- mixed gases are ideal.

The inlets of zinc and oxygen source both are set as velocity-inlet; Inlet Wall is set as the constant temperature 573K; Inner Wall is set as insulated boundary condition; Rotating Substrate is set as the constant temperature 743K, and at the rotational speed of 750rpm; The gas outlets are set as pressure-outlet; the operating pressure is 11torr.

#### 4.3 SIMULATION OF ZNO DEPOSITION RATE AND EXPERIMENTAL VERIFICATION

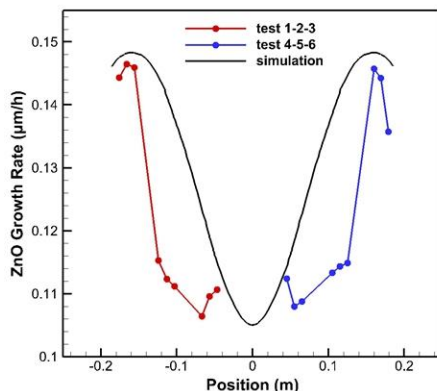
Experiments are performed base on corresponding parameter to simulation condition above. We got 12 pieces of ZnO epitaxial wafer, and adopted N&K film thickness gauge to measure the thickness of thin film by reflectance and refraction by the wavelength at the range of 190nm to 1000nm.

As shown in the **Figure 5**, 4 lines are selected cross the center of graphite susceptor, and 9 sampling points are picked in each line to measure the thickness of film.



**Figure 5** Map of sampling points

In this section, we compare average depositions in experiment with simulation (see **Figure 6**), and find out simulation deposition rate distribution curve generally coincides with the experimental distribution curve, which validates reliability of our numerical model and illustrates the model accurate. There will exist a short shift on growth results measured by N&K film thickness gauge, so we verify the tendency on simulations and experiment results.

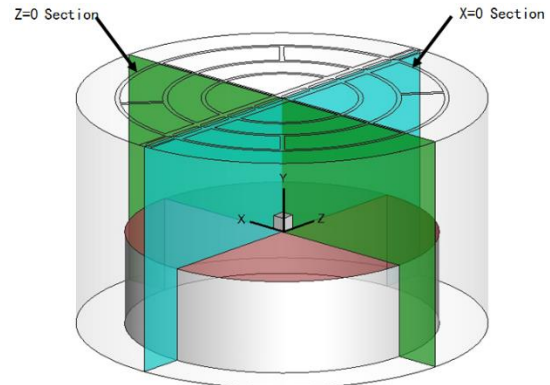


**Figure 6** Comparison of ZnO growth rates of experiment and numerical simulation

(The origin of coordinates is the center of graphite susceptor;)

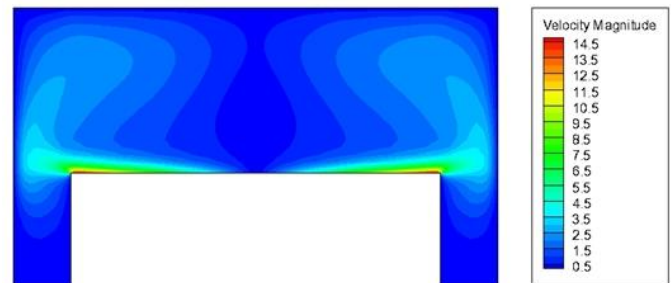
#### 4.4 RESULT AND ANALYSIS

In order to analyze distribution of temperature and velocity field in the reactor, two orthogonal cross-sections are picked,  $X=0$  and  $Z=0$ , as shown in **Figure 7**. Furthermore,  $X=0$  section is perpendicular to the plane of zinc source inlets.

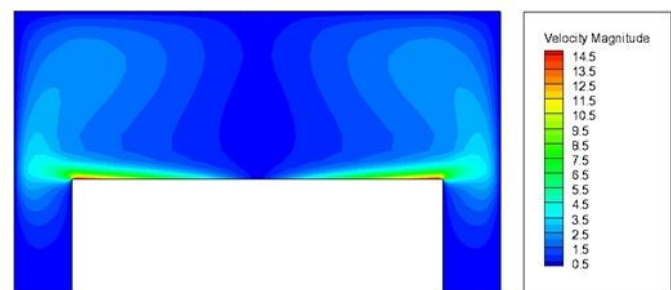


**Figure 7** Section  $X=0$  and section  $Z=0$

##### 4.4.1 ANALYSIS OF VELOCITY FIELD IN THE REACTOR



(a) Section  $X=0$

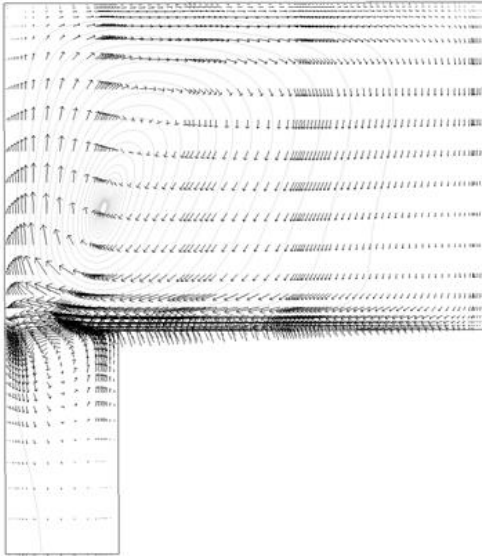


(b) Section  $Z=0$

**Figure 8** Velocity contour

From **Figure 8**, there is the maximum velocity of gases mixture above the surface of graphite susceptor quite greater than gases flow near inlets, which is co-action of thermal buoyancy effect and pumping effect driven by high rotational speed of graphite susceptor. Pumping effect is the coupled outcome of viscosity force and centrifugal force driven by high rotational speed. For the reason of viscosity force, a layer of gases near the surface of substrate pursuit movement of the spin. And gases will be pulled to the edge of spin. At the same time,

gases mixture above the spin will replenish through a layer above spin surface. So at proper rotation speed, graphite susceptor can not only make gases flow stable through substrates, but also improve the uniformity of temperature field above spin. There exist a swirl (see **Figure 8**), generated by the coupled effect of thermal buoyancy effect and low velocity of gases near inlets (see **Figure 9**).



**Figure 9** Velocity vector at section X=0 (left side)

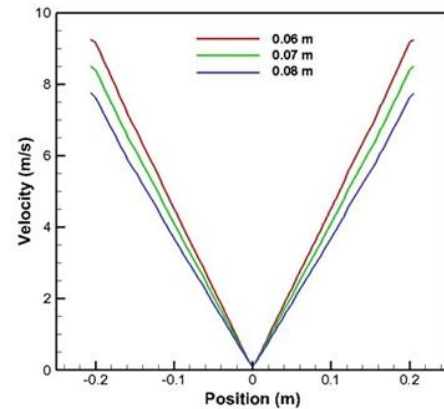
Reactant molecules and film precursor diffuse through boundary layer to substrate surface and adsorb, then take place solid phase chemical reaction and produce reactive group of exipital film material and by-product. Then molecular groups form into critical nucleus, diffuse on the growth surface, grow into crystal lattices and form into consecutive thin film at last. Generally recognizing, reactions outside boundary layer are pre-reactions. Normally the width of boundary layer of ZnO thin film is 0.11m [9-10], namely there exist pre-reactions outside the zone of boundary layer 0.11m possibly. For this reason, we pick 3 lines above the surface of graphite susceptor at the height of 0.06m, 0.07m, 0.08m, respectively (see **Figure 10**) and investigate the distribution of gases velocity.



**Figure 10** Schematic of picked line position

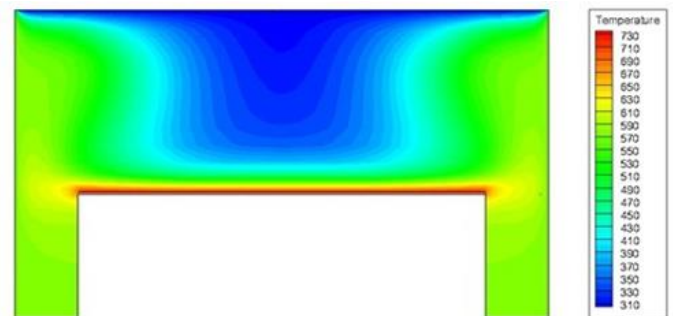
The distribution of flow velocity at the height of 0.06m, 0.07m, 0.08m above the graphite susceptor is shown as **Figure 11**. The flow velocity is proportional to the distance from the

center of graphite susceptor. The flow velocity at the center of graphite susceptor is near zero. In other words, the flow velocity is quite large, except the velocity above the center of graphite susceptor. This also illustrates the phenomenon, low ZnO deposition rate inside the inner circle of the graphite susceptor for the consumption of raw materials being not promptly replenished.

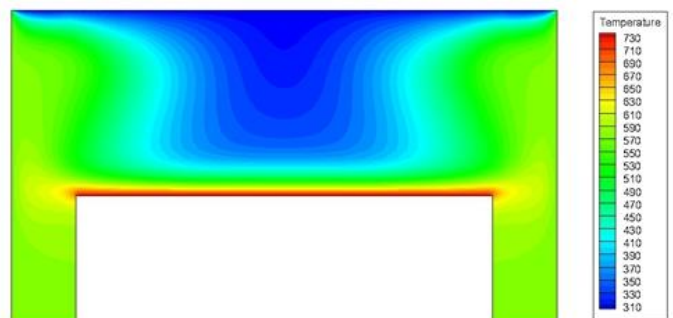


**Figure 11** Velocity at the heights of 0.06m, 0.07m, 0.08m upon the Substrate

#### 4.4.2 ANALYSIS OF TEMPERATURE FIELD



**(a)** Section X=0



**(b)** Section Z=0

**Figure 12** Temperature contour

The field of flow comes into being by coupled effects of gases velocity, pumping effect generated by rotational susceptor and thermal buoyancy generated by high temperature of susceptor. So the flow field exhibits a concave profile, low temperature in the center zone of reactor and high temperature in

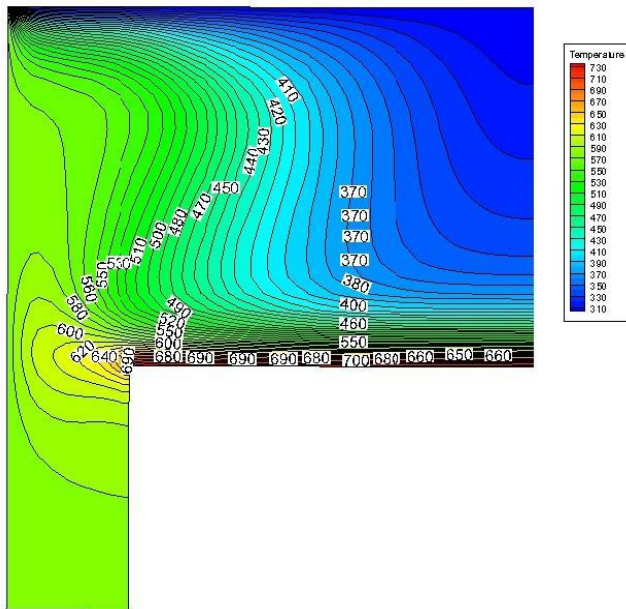
the zone near out wall. In addition, it is reported that the growth temperature is 633K to 773k, using DEZn and O<sub>2</sub> as source material by the method of MOCVD [11]. Normally the first step of pre-reaction is decomposition reaction of reactant. The decomposition temperature condition of DEZn is list below in table 1, according to related record [12].

**Table 1** Zn(CH<sub>3</sub>)<sub>2</sub> decomposition reaction

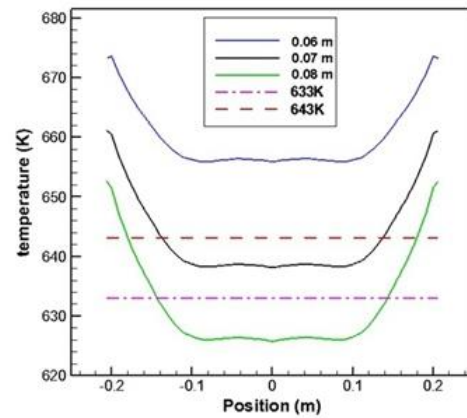
$Zn(CH_3)_2 = ZnCH_3 + CH_3$		
Temperature T (k)	Factor A	Activation Energy Ea (KJ/mol)
643	6.0E+5	22,000
743	6.5E+10	94,999

In order to make the map of temperature specific, the map of temperature contour is made at the left side of X=0 section, as shown in **Figure 13**. From the map below, we find there exist only a very thin layer of zone meeting require of the temperature 633K to 643K. What we care about is the zone between the inlets and the graphite susceptor, where pre-reaction takes place. We pick 3 lines above the surface of graphite susceptor at the heights of 0.06m, 0.07m and 0.08m, respectively (see **Figure 10**) and investigate the distribution of temperature (see **Figure 14**). DEZn decomposition reaction meeting require of temperature 643K is taken place at the height of 0.06m to 0.07m. DEZn combination reaction meeting require of temperature 633K is taken place at the height of 0.07m to 0.08m.

The analysis above shows that it exists pre-reactions for meeting requirement of gases velocity and temperature on a thin layer on the graphite susceptor.



**Figure 13** Temperature contour of left section Z=0



**Figure 14** Temperature at the heights of 0.06m, 0.07m, 0.08m above substrate

## 5. CONCLUSIONS

1. Simulation deposition rate distribution curve generally coincides with the experimental distribution curve, which validates reliability of our numerical model and illustrates the model accurate. Simulation results present that the deposition rate increases with the increase of the radial distance within 0.16m from susceptor center. But after 0.16m the deposition rate shows downtrend. This is effect caused by the consumption of MO source.

2. By analyzing the distribution of velocity in MOCVD reactor, results show that gases velocity at the center is small, which illustrates the low deposition rate at the center of susceptor for consumption of raw materials being not promptly replenished.

3. By analyzing the distribution of temperature, velocity, mass fraction, deposition rate and the pre-reaction conditions, there exists a zone of pre-reaction within the height of 0.07m. In order reduce pre-reaction, increasing MO source velocity and increasing rotational speed of the susceptor are suggested.

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