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NUMERICAL SIMULATION OF THE DEPOSITION PROCESS AND THE EPITAXIAL GROWTH OF CADMIUM TELLURIDE THIN FILM IN A MOCVD REACTOR

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ABSTRACT

Metalorganic Chemical Vapour Deposition (MOCVD) is an attractive method for depositing thin films of cadmium telluride (CdTe) and other group II-VI compound materials. It has been known that the growth rate of CdTe thin film is sensitive to the substrate temperature and the reactant partial pressures, indicating that the deposition process is kinetically controlled and affected by many conditions. In the deposition process, heterogeneous reactions play an important role in film formation and the process is further complicated by the coupling of gas and surface reactions via desorption of the reactive intermediates. A detailed understanding of the deposition mechanism and kinetics will be crucial for the design, optimization and scale-up of II-VI MOCVD reactors. This paper presents the results of CFD modelling of the deposition process in an inline MOCVD reactor, taking into account the heat transfer and mass transport of the chemical species. The numerical simulations have been conducted using the CFD code, ANSYS FLUENT. The influence of the process controlling parameters such as total flow rate, reactor pressure and substrate temperature on the deposition behaviour has been assessed. In the present study, dimethylcadmium (DMCd) and diisopropyltelluride (DiPTe) have been used as precursors while H_2 is acting as the carrier gas and N_2 as the flushing gas. The capabilities of using the developed CFD models for revealing the deposition mechanisms in MOCVD have been demonstrated. The simulations have been conducted in both mass transport and kinetics regimes at the temperature range of 355-455° to match the experimental conditions.

INTRODUCTION

Metalorganic chemical vapour deposition (MOCVD) is currently one of the most important techniques for thin films with applications in electronics, optics and thin film photovoltaic solar cells [1]. Its processing has many advantages such as low-temperature, radiation damage-free deposition, selective deposition, and film stress and grain size control, allowing the growth of uniform and high quality thin films. Models that relate the deposition rate, uniformity, film composition of the MOCVD process to operating conditions (such as reactor geometry, reactant species concentration, flow rates, temperature gradients, etc.) will be useful for predicting the performance of existing reactors, and can also provide optimal designs for new reactors for a given process [2]. As a key step, fundamental understanding of the deposition process of CdTe, as a well-established material used for fabrication of photovoltaic solar cells, is crucial to realisation of a successful MOCVD process. Since the MOCVD process is critically dependent on the fluid dynamics of the reacting and carrier gases, quantitative and qualitative understanding of basic fluid dynamics associated with the adopted MOCVD reactor is the key to achieve improvements in efficiency, crystal production and growth uniformity. Nevertheless, there are several problems which still remain unresolved because a number of parameters involved in MOCVD have a significant impact on the necessary uniformity and reproducibility, and how they are correlated are not fully understood.

The design of MOCVD processes and related equipment is currently largely based on empirical experience. However, to gain such experience via "trial and error" experimentation is usually expensive and time-consuming. Although empirical and semi-empirical models have been developed, these models have a limited range of applicability, and changes in reactor design can further limit their use [3,4]. A better approach for developing quantitative understanding of process dynamics and predicting MOCVD reactor behaviour under a wide variety of conditions is to develop robust physically based methods using CFD modelling approach [5,6].

The aim of this paper is to investigate the influence of the process controlling parameters such as total flow rate, reactor pressure and substrate temperature on the deposition behaviour of an inline MOCVD reactor using CFD modelling. The numerical simulations have been conducted using the CFD code, ANSYS FLUENT [7], taking into account the heat transfer and mass transport of the chemical species, at a range of temperatures. Dimethylcadmium (DMCd) and diisopropyltelluride (DiPTe) have been used as precursors while H_2 is acting as the carrier gas and N_2 as the flushing gas.

There are limited studies on modelling of the CdTe epitaxial growth and only few models have been developed to analyse and predict the growth rate. Liu *et al.* [8,9] and McDaniel et al. [10,11] employed a boundary-layer model incorporating a catalytic reaction to simulate the kinetics of CdTe deposition in a tubular reactor and studied the reaction chemistry of CdTe using on-line gas chromatography and numerical simulation. Irvine et al. [12] have explored the reaction mechanism of CdTe with a kinetic model based on their experimental results obtained by using reflectometry, covering the range from low to high temperatures. They have revealed that the surface catalysis of tellurium organometallics bound to group II surface atoms is the dominant process in low temperature while the tellurium desorption occurs in high temperature regime. Kuhn *et al.* [13] have conducted two-dimensional numerical simulation using CFD code – Fluent to investigate the hydrodynamics in a horizontal MOCVD reactor. Tena-Zaera *et al.* [14] also developed a 2-D model to simulate the gas flow and predict the CdTe deposition in a horizontal MOCVD reactor, coupled with heat transfer and mass transport of the chemical species. They have significantly simplified the chain of reactions presented in the CdTe deposition process and proposed to adopt a global surface reaction. However, their simulations were not compared with the experimental data and it is hard to trace whether or not the pre-exponential factor and activation energy used in their surface reaction kinetics are appropriate.

The present study has employed a full three-dimensional CFD model to simulate the CdTe deposition process in an in-line MOCVD reactor. The CFD code – ANSYS Fluent [7] has been adopted to conduct the simulations. In the simulations, heat transfer and mass transport of the chemical species have been taken into consideration. The effects of controlling parameters such as reactor pressure, partial pressures of precursors, total carrier gas flow rate and substrate temperature on the hydrodynamics in the reactor and CdTe growth rate are analysed and carefully assessed. The precursors used in the modelling are diisopropyltelluride (DiPTe) and dimethylcadmium (DMCd), which are the precursors for the MOCVD CdTe growth experiments in CSER, OpTIC Glyndŵr for substrate temperature ranging from 355 to 455 ºC [18]. The carrier gas is hydrogen.

This paper is organised by presenting mathematical modelling for description of flow dynamics in the MOCVD reactor in Section 2. Section 3 describes numerical simulation details of the MOCVD system, while the numerical results, comparisons with the experimental data and discussion are given in Section 4. The last section presents the conclusions drawn from the present study.

NOMENCLATURE

A_r	[s^{-1}]	Pre-exponential factor
C	[kmol/m^3]	Molar concentration
c_p	[J/(kg·K)]	Heat capacity
D	[m^2/s]	Binary diffusion coefficient
D_T	[m^2/s]	Thermal mass diffusion coefficient
E	[kJ/mol]	Characteristic energy potential
E_r	[J/mol]	Activation energy
$\boldsymbol{g}$	[m/s^2]	Gravity acceleration
h	[J/mol]	Enthalpy
J	[kg/(s·m^2)]	Diffusion mass flux vector
M	[g/mol]	Molecular weight
M_w	[g/mol]	Local average molecular weight
N	[-]	Number of chemical species
P	[Pascal]	Reactor pressure
$\boldsymbol{q}$	[J/m^2·s]	Heat flux vector
R	[8314J/kmol·K]	Ideal gas constant
R	[mol/(dm^3·s)]	Net rate of creation of mass
R_{is}	[mol/(dm^3·s)]	Rate of surface deposition
T	[K]	Temperature
$\boldsymbol{U}$	[m/s]	Velocity vector of gas
U_n	[m/s]	Velocity normal to the deposition surface
Y	[-]	Mass fraction

Special characters

α	[-]	Coefficient of thermal expansion
η	[-]	Rate exponent
λ	[W/(m·K)]	Thermal conductivity
μ	[kg/(m·s)]	Viscosity
ν	[-]	Stoichiometric coefficient
ρ	[kg/m^3]	Gas mixture density
σ	[m]	Value of the Lennard-Jones diameter
τ	[Pa]	Viscous stress tensor

Subscripts

W	Weight
b	Backward
$crit$	Critical
D_h	Hydraulic diameter
f	Forward
i	Species i
j	Species j
n	Normal
r	Reaction
s	substrate
w	wall

MATHEMATICAL MODELLING

The MOCVD process involves various transport phenomena such as gas flow, heat transfer, and mass transport, where CFD modelling of the MOCVD process requires a set of governing equations that are used to express conservation of energy, mass, momentum, and chemical species [15].

In deriving these conservation equations the following assumptions have been introduced:

(i) The gas mixture can be treated as a continuum (here the Knudsen number is small for CdTe deposition at the normal temperature range of 355 - 455 ºC with the static pressures around 760 Torr).

(ii) The equation of state is assumed to obey the ideal gas law.

(iii)The gas flow in the MOCVD reactor is laminar. (The Reynolds number based on the hydraulic diameter in most of MOCVD systems usually falls into the range of 1 to 100, which is well below the values at which turbulence is expected.)

(iv) Only steady state simulations are conducted because the film growth rate is slow compared to the average carrier gas velocity in the reactor. Therefore, the time derivatives in the momentum, energy, and species balance expressions can be dropped.

Under these assumptions, the governing equations describing CdTe deposition process can be written:

Conservation of Mass

$$\nabla \cdot (\rho \boldsymbol{U}) = 0 \tag{1}$$

where ρ is the gas mixture density and $\boldsymbol{U}$ is the velocity vector of gas. The density of the gas mixture can be evaluated using the ideal gas law

$$\rho = \frac{PM_w}{RT} \tag{2}$$

where P is the reactor pressure, T is the temperature of the deposited surface, R is the ideal gas constant and M_w represents the local average molecular weight, which can be calculated using the local mass fractions of the species and their corresponding molecular weights.

Conservation of Momentum

$$\nabla \cdot (\rho \boldsymbol{U}\boldsymbol{U}) = -\nabla P - [\nabla \cdot \tau] + \rho \boldsymbol{g} \tag{3}$$

where τ is the viscous stress tensor and $\boldsymbol{g}$ is the acceleration due to gravity.

Conservation of Energy
There exists a very steep thermal gradient perpendicular to the substrate surface in the MOCVD reactor. Thus, the transport equation for thermal energy needs to be included in the modelling. The equation describing the energy balance for gas mixture in terms of the temperature can be written

$$\begin{aligned} c_p \frac{\partial \rho T}{\partial t} &= -c_p \nabla \cdot (\rho \boldsymbol{U} T) + \nabla \cdot \boldsymbol{q} + \frac{DP}{Dt} - \tau : \nabla \boldsymbol{U} \\ &- \sum_{i=1}^{N} \sum_{j=1}^{K} h_i \nu_{ir} \left(R_r^f - R_r^b \right) + \Delta E_r \end{aligned} \tag{4}$$

where c_p is the heat capacity at constant pressure, $\boldsymbol{q}$ is the molecular heat transport vector, h_i is the enthalpy of species i, ν_{ir} is the stoichiometric coefficient in reaction r. The first term on the right side is the rate of energy due to convective transport. The second term represents the energy increase due to molecular transport mechanisms, and third term is the energy increase due to compression. The quantity, $-(\tau{:}\nabla \boldsymbol{U})$, denotes the viscous dissipation heating, which is small for MOCVD reactor and can be neglected in the modelling. Finally, ΔE_r represents radiative energy transport, which can be also neglected.

Chemical Species Transport Equation
The conservation equation for each chemical species in the fluid mixture can be expressed as

$$\nabla \cdot (\rho \boldsymbol{U} Y_i) = -\nabla \cdot \boldsymbol{J}_i - [\nabla \cdot \tau] + R_i \tag{5}$$

where Y_i is the mass fraction of species i in the gas mixture, and R_i is the net rate of creation of mass of species i, $\boldsymbol{J}_i$ is the diffusion mass flux vector for species i. Using the ideal gas approximation and assuming small pressure gradients, and dilute concentration of reactants in the carrier gas, the diffusion mass flux of species i in the carrier fluid can be expressed as

$$\boldsymbol{J}_i = -\rho D_i \nabla Y_i - D_i^T \frac{\nabla T}{T} \tag{6}$$

where D_i is the binary diffusion coefficient of species i in the carrier gas and D_i^T is the thermal mass diffusion coefficient for species i in the carrier gas. The second term, on the right hand side of equation (6), represents the thermal diffusion effect.

In order to define the problem for a particular reactor configuration, the above transport equations must be completed with suitable boundary conditions at inlet and outlet of the MOCVD reactor. When surface reactions are taken into account, the gas-phase mass flux of each species to the surface is balanced by the creation or destruction rate of that species by heterogeneous reactions. Such flux balanced for species i can be written

$$\rho U_n Y_i + \boldsymbol{J}_i \cdot \boldsymbol{n} = R_{is} \tag{7}$$

where U_n is the velocity normal to the deposition surface, $\boldsymbol{n}$ is the unit vector normal to the surface, and R_{is} is the rate of surface deposition of species i. Temperature boundary conditions at the reactor walls can be defined by assuming a constant temperature due to introduction of a cooling measure. The temperature boundary condition for the substrate can be defined being either a constant or a conduction wall. In the simulations, "no-slip" condition has been imposed to all the reactor walls. The distributions of velocity, temperature, and component mass fractions are defined at the reactor inlet. At the outlet of the reactor, a zero normal gradient condition is applied for total mass flux vector, as well as zero heat and species diffusion fluxes.

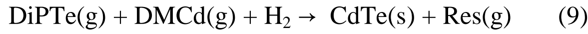
When applying Equation (6) to determine the diffusion mass

flux of species i in the carrier fluid, the binary diffusion coefficient of species i, D_i and the thermal mass diffusion D_i^T have to be provided. The expression of the diffusion coefficient, with errors typically within 5-10%, is given by [16]:

$$D_{ij} = 0.0188\sqrt{\frac{1}{M_i} + \frac{1}{M_j}}\,\frac{T^{3/2}}{P\sigma_{ij}\Omega_{D,ij}} \tag{8}$$

where M_i and M_j are, respectively, the molecular weight of species i and j, P is the reactor pressure, σ_{ij} is the mean value of the Lennard-Jones diameters of species i and j [19]. $\Omega_{D,ij}$ is the collision integral for diffusion and is a function of the parameter kT/ε_{ij} with $\varepsilon_{ij}=(\varepsilon_i\varepsilon_j)^{1/2}$, where ε_i and ε_j are the characteristic energy potential of species i and j, respectively. For CdTe deposition in the MOCVD reactor, the second term of Equation (6) can be neglected because the thermal diffusion coefficient D_i^T is usually very small (i.e. D_{DiPTe}^T, D_{DMCd}^T << $D_{DiPTE,H2}$, $D_{DMCd,H2}$) and the mass diffusion due to thermal gradients (Soret effect) is ignored in the modelling.

The solution of governing equations (1) to (6) is coupled with the evaluation of surface reactions on the substrate. Due to the lack of the detailed chemical data regarding the deposition of CdTe film from the gas mixture, one overall surface chemical reaction on the substrate was considered.



$$\text{DiPTe(g)} + \text{DMCd(g)} + H_2 \rightarrow \text{CdTe(s)} + \text{Res(g)} \tag{9}$$

where Res(g) represents the by-products. The following Arrhenuis expression is used to expressed the rate (R_{ir}) of the reaction

$$R_{ir} = \nu_{ir} M_i A_r e^{-\frac{E_r}{RT}} \prod_{j=1}^{N_r} \left[C_j\right]^{\eta_{j,r}} \tag{10}$$

where C_j is the molar concentration of specie j, A_r is the pre-exponential factor which indicates the frequency of reaction between the precursor molecules, E_r is the activation energy that takes into account the minimum amount of energy to initiate the reaction. N_r is the number of chemical species in reaction r and $\eta_{j,r}$ is the forward rate exponent for each reactant and product species j in reaction r.

As can be seen from Equation (5), the film deposition or growth is determined by two consecutive processes, the diffusion due to mass gradient and surface reaction. The growth rate will be mainly determined by the controlled process parameters. When there exists a strong mass gradient on the substrate, the growth rate is likely to be controlled by the arrival of the constituents to the substrate, i.e. the growth takes place in a mass transport regime. When surface reaction becomes dominant, the growth will be decided by reaction kinetics. The criteria to judge the dominant growth regime is to investigate the dependence of the growth rate on the substrate temperature [17]. Generally speaking, if the growth rate is proportional to $T^{3/2}$, as the diffusion coefficient defined in Equation (8), the dominant deposition will be mainly controlled by the mass transport. On the contrary if the temperature dependence follows an exponential form, as seen in Equation (9), i.e. $\propto\exp(-E_r/RT)$, the reaction kinetics will become dominant for the deposition.

MODEL DESCRIPTION AND NUMERICAL SIMULATION

CFD simulations have been conducted based on an in-line atmospheric pressure (AP-) MOCVD reactor in which the CdTe thin films were deposited on 0.7 mm thick Corning Eagle 2000 aluminosilicate glass substrate of 5×7.5 cm^2. Precursors were assumed to be released normal to the substrate, which can be stationary or moving as shown in Figure 1.[19] The reactor consists of a rectangular block reaction cell with the size of 7.5×7.0×1.35 cm^3 and an injection head where the precursors and carrier gas were introduced. Inside the reactor, the substrate is heated by resistive heater cartridges, to obtain the required temperature for the pyrolysis of metalorganic precursors. These conditions are also adopted in our CFD modelling.

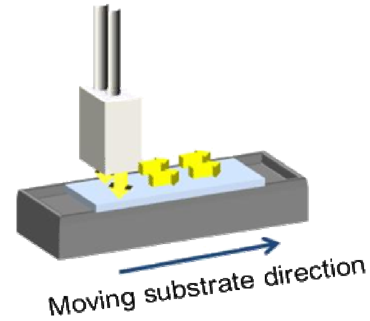


Figure 1. Schematic of inline AP-MOCVD process employed to grow CdTe thin films. The substrate can be stationary or moving at speeds up to 2.25 cm/min in the experiments and CFD modelling.

As clearly indicated in governing equations (1) to (6), the chemical species transport, i.e. CdTe deposition process, is strongly affected by hydrodynamics and heat transfer occurring in the MOCVD reactor while the hydrodynamics can be characterised by the Reynolds number. A preliminary analysis of the flow regimes and characteristics of the gas mixture flow, in the inline reactor, is of interest in order to evaluate the possibility to incorporate some simplifications in the numerical simulations. To determine the type of flow, i.e. laminar or turbulent, the Reynolds number based on the hydraulic diameter of the reaction cell was calculated [16]:

$$\mathrm{Re}_{D_h} = \frac{\rho_{H_2} U_{reactor} D_h}{\mu_{H_2}} \tag{11}$$

where ρ_{H2} is the fluid density, $U_{reactor}$ is the gas mixture average velocity, D_h is the reactor hydraulic diameter and μ_{H2} the carrier

gas H_2 viscosity. The estimated Re_{Dh} are falling into between 4 and 33, depending on the range of temperature and total gas flows used in the modelling. These values are significantly smaller than the critical Reynolds number (~2300), indicating the flow in the reactor is overwhelmingly laminar. It should be noted here that the calculation of the Reynolds number strictly requires the physical properties of the gas mixture. However, only carrier gas H_2 has been used for estimation of the Reynolds number because the concentration of precursors is very small in comparison to that of H_2.

In the CdTe deposition experiments, the temperature of the substrate is much higher than that on the reactor walls. This may give rise to a strong free convection and buoyancy-induced flows inside the reactor. It is necessary to estimate the Rayleigh number (*Ra*) [16] so as to identify whether or not the effect of free convection occurring in the inline reactor has to be taken into account in the CFD modelling.

$$Ra = \frac{\alpha g c_p \rho^2 D_h^3 \left(T_{Sub} - T_W\right)}{\mu \lambda} \qquad (12)$$

where α is the coefficient of thermal expansion, g is the gravity acceleration. T_{Sub} and T_W are, respectively, the temperatures of the substrate and reactor walls. λ is the thermal conductivity of the carrier gas. The Rayleigh number (Ra) was also evaluated for values of the H_2. The wall temperature was assumed to be 16 ºC (289 K) while the substrate temperature varies in the range of 355 to 455 ºC in both the experiments and CFD modelling. The calculated Rayleigh number was found ranging from 1 to 10 in the present study. These values are very much lower than the critical Rayleigh number (Ra_{crit}=1700), indicating the effect of free convection is weak [16]. However, the free convection of the gas flow is still taken into account in this study for caution.

In the simulations no-slip boundary conditions were imposed on the reactor walls. The exit of the reactor was defined as pressure outlet at the reactor pressure. The inlet of the injector was defined as velocity inlet with the velocity being specified based on the carrier gas and precursors flow rate and specification of mass fractions of precursors. In addition, the inline AP-MOCVD reactor walls have been approximated as isothermal walls since an effective water cooling system has been employed in the actual experiments. A constant temperature condition has been applied to the substrate surface. Pressure-velocity coupling was obtained using the Semi-Implicit Method for Pressure Linked Equations (SIMPLE) algorithm, the discretisation scheme for pressure was second-order, and the scheme for momentum and energy together chemical species transport was the first order upwind to ensure stability. The convergence criteria were that, for all parameters, the residuals were less than 10^{-5}. All simulations were conducted using the commercial CFD software ANSYS Fluent 6.3.26.

The simplified model of the inline AP-MOCVD reactor and the mesh system used in our CFD modelling are shown in Figure 2. The computational domain used in the modelling for defining the whole reactor contains 426,000 cells. Since the deposition process is strongly influenced by the temperature gradient and boundary layer formed on the substrate, a fine mesh in the vicinity of the substrate has been employed. Further refinement on the mesh used in the simulation has been tested but it was found, from the trial simulation that the results almost remain unchanged.

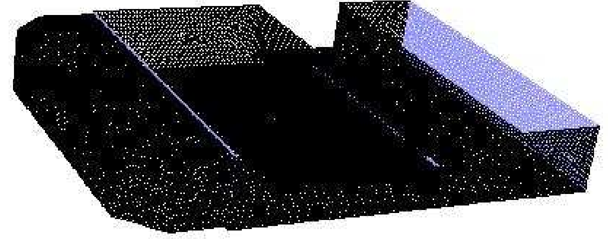


Figure 2. Schematic of the reactor and computational grid.

RESULTS AND DISCUSSION

Numerical simulations have been conducted to investigate the effects of the gas mixture flux, substrate temperature and partial pressure conditions on the CdTe deposition hydrodynamics and the film growth in the in-line AP-MOCVD reactor. To look into the film growth rate, an area weighted average on the calculated growth rate of CdTe deposited on the substrate has been taken. The simulations have covered low to middle substrate temperature range which may include the optimum range for the CdTe film growth [18].

Effect of substrate temperature on growth rate

In order to evaluate the effect of substrate temperature on the CdTe growth rate, the substrate temperature was varied from 355ºC to 455 °C. The previous study [12] on CdTe deposition has revealed that there exist two dominant processes, mass transport limited and kinetic limited, which are significantly affected by the temperature. In the simulations, the Arrhenius parameters have been estimated based on experimental data [19]. VI/II ratio has been kept to be equal to 0.55.

Figure 3 shows the area weighted average CdTe growth rate on the substrate as a function of the inverse substrate temperature, ranging from 355 to 455 ºC. It can be seen from the figure that for the whole temperature range, the growth rate decreases as the temperature decreases. However, the dependence of the growth rate on the temperature seems to exhibit different behaviour for different temperature range. In relatively low temperatures ranging from 355-405 ºC, the predicted growth rate can be well approximated by Arrhenius equation, clearly

indicating that the CdTe deposition is strongly dominated by reaction kinetics. In the temperature range of 405 to 455 ºC, the two processes, mass transport limited and kinetic limited, are coexisting. When the temperature is higher than 405ºC, the increase of growth rate is obviously slow down and the temperature dependence seems to be approximated by a temperature power law, which can be thought of being mainly affected by mass diffusion transport. Further increase in the temperature may cause desorption of molecules from the epitaxial surface as pointed out by Irvine et al. [12].

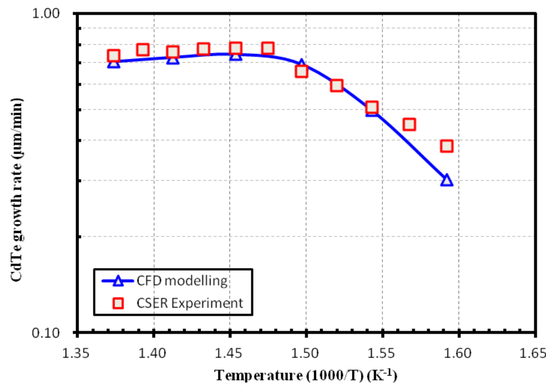


Figure 3. CdTe growth rate on the substrate versus inverse temperature. CFD modelling conditions: P_{DiPTe} = 1.1×10^{-3}atm, VI/II ratio = 0.55, Total flux = 0.5 l/min, P = 950 mbar.

Effect of the total flux on CdTe growth rate

In the inline AP-MOCVD growth experiment, the parameters that appear to be more directly related to the film growth rate are the total flux and the partial pressure of precursors. For the experiments conducted in CSER, the partial pressure of precursors was fixed at a certain value and the total flux was changed to examine the effect of the total flux of gas flow on the growth rate. This effect was also assessed using CFD modelling. In the simulations, the total flux as a parameter varies from 0.5 to 1.5 l/min. The partial pressures of both precursors were maintained at constant values with 1.1×10^{-3} atm for DiPTe and 2.0×10^{-3} atm for DMCD while the substrate temperature is maintained to be 395 ºC. The calculated CdTe growth thickness variation with the total flux is shown in Figure 4. It can be seen clearly from Figure 4 that the CdTe growth rate increases with increase of the total flux, which is consistent with the experimental observation and measurement. However, the increase rate tends to be higher than the experimental one for higher total flux. This may be attributed to the use of an over-estimated value of the pre-exponent factor in Arrhenius equation (10) in the modelling. Apparently, A_r should be dependent on the temperature. It is also interesting to note that the numerical simulation can at least qualitatively predict the uniformity of the growth rate along the substrate as shown in Figure 5. It was revealed, from Figure 5, that the overall uniformity trend remains almost invariant for different total fluxes when the partial pressures of precursors were fixed. This result likely indicates that the variation in the total flux has little impact on the CdTe deposition uniformity when the precursor partial pressures are maintained to be certain values. This can be explained by the fact that an increase in the total gas mixture flux will give rise to increase in the average velocity in the reactor so that the local growth rate along the whole substrate is entirely enhanced without altering the uniformity. As the growth rate contributed by mass transport limited is approximately proportional to the gas velocity, i.e.

$$R_i \propto T^{1/2} \sqrt{U_{reactor}} \qquad (13)$$

the local growth rate contributed due to the surface reaction as a function of the position will not change significantly when the substrate temperature is kept unchanged. While the flux increase gives rise to the change of the thickness of the velocity boundary layer formed on the substrate, the boundary layer distribution along the substrate does not change significantly so that the growth rate uniformity is not remarkably influenced by the total gas mixture flux. The only difference that can be observed from the simulations is that the CdTe growth thickness changes with the total flux. This result is also consistent with the experimental data and previous study as reported by Tena-Zaera *et al.* [14].

It should be noted here that the uniformity of the CdTe thin film on the substrate will be influenced by the design of the reactor because the boundary layer formed on the substrate is significantly affected by the flow features in the reactor.

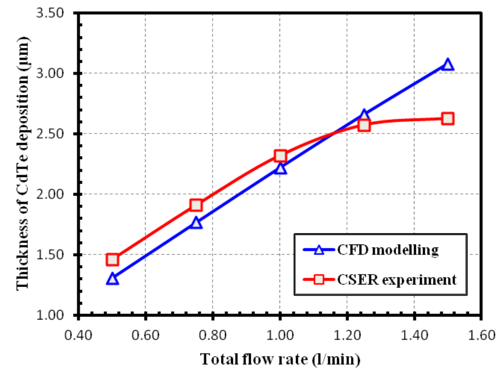


Figure 4. CdTe growth thickness variation with the total flux. CFD modelling conditions: P_{DiPTe} = 1.1×10^{-3}atm, VI/II ratio = 0.55, Total flux = 0.5 l/min, P = 950 mBar.

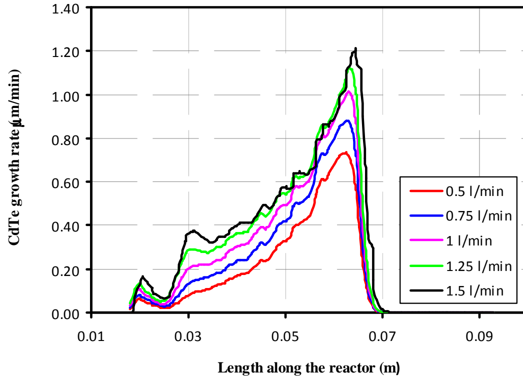


Figure 5. CdTe growth rate distribution along the length of the substrate for different values of total flux. P_{DIPTe} = 1.1×10^{-3}atm., VI/II ratio = 0.55, P= 950 mbar and T_{sub} = 395ºC.

Figure 6 shows the comparison of the predicted CdTe deposited mass to the experimentally measured deposition mass for different total flux. Both carrier gas and precursor flows were increased to yield total flows up to 1.5 l/min. It can be seen from the figure that the predicted deposition mass is in general agreement with the experimental data. In order to evaluate the efficiency of CdTe material utilisation in the CdTe deposition using CFD modelling, one can define the material utilisation, U_{mat}, as proposed by Barrioz et al. [19]:

$$U_{mat} = \frac{m_{CFD}}{m_{theor}} \times 100\% \quad (14)$$

where the theoretical mass of deposit, m_{theor}, limited by the molar supply of the limiting metalorganic precursor, can be estimated by

$$m_{theor} = \rho_{CdTe} \frac{P_{mo} \dot{M}_{mo} N t_d}{22.4} \frac{a_0^3}{2} \quad (15)$$

where P_{mo} and M_{mo} are the partial pressure and the mass flow rate of the limiting precursor, t_d is the deposition time, N denotes Avagadro's number, a_0 is the lattice parameter (i.e. 6.48 Å for CdTe) and ρ_{CdTe} is the density of CdTe. It can be seen from the figure although thicker film thickness can be obtained at higher flow rates, the material utilisation reduces greatly (by up to ~18 % as the total flow is tripled). A strong decrease in materials utilisation with increasing flow rate is expected for kinetically limited growth where the deposition rate will depend on concentration and not on the molar flow rate. Thus, it is clearly indicated in Figure 6 that using smaller total flows and higher precursor concentrations may be effective when considering the efficiency in materials consumption.

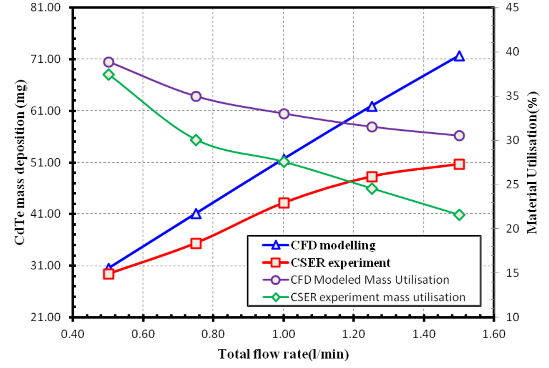


Figure 6. CdTe deposited mass variation with total flux. VI/II ratio = 0.55, P = 950 mbar and T_{sub} = 395 ºC.

Effect of the reactor pressure on CdTe growth rate

As can be seen from Equation (6), the film growth rate is influenced by the mass diffusion flux which is also strongly associated with the mass diffusion coefficient. Equation (8) has clearly indicated that

$$D_{ij} \propto \frac{1}{P} \quad (16)$$

when other controlling parameters are kept unchanged. Thus, one would expect that the reactor pressure will remarkably influence the film growth rate, especially when the system is working in the mass limited diffusion regime and the molar fractions of precursors are maintained to be unchanged. In order to evaluate the influence of reactor pressure on the CdTe growth rate in the inline AP-MOCVD reactor, simulations of the growth rate on the substrate using the reactor pressure as a controlling parameter have been conducted. The total flux and the molar fractions of the precursors have been kept constant, and the reactor pressure varied from 350 mbar to 950 mbar. The predicted CdTe growth rates for different reactor pressures are shown in Figure 7. It can be seen from the figure that with decrease in the reactor pressure, the CdTe growth rate decreases remarkably. This result is in contradiction to the expectation. When the partial pressures of precursors are fixed, the molar fractions of the precursors increase, when the total reactor pressure decreases. In the present case, the partial pressures of DiPTe and DMCd are kept unchanged, the CdTe growth rate should increase with decrease in the reactor pressure. A very like explanation to the simulation result is that the deposition process has been dominated by kinetics limited. Further investigation is needed. It should be noted here that although the current simulations are concerned with the inline AP-MOCVD, the result will be beneficial to the design of new inline AP-MOCVD reactors.

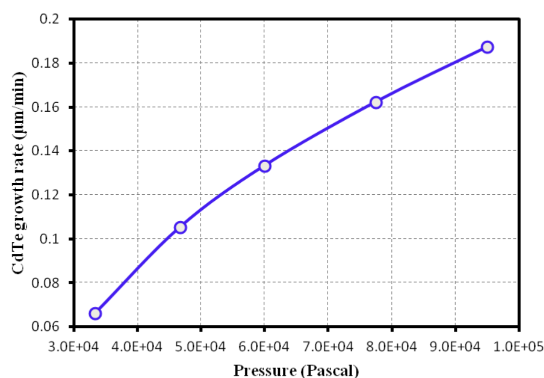


Figure. 7. CFD modelling of CdTe growth rate dependence on the reactor pressure. $P_{DIPTe} = 1.1\times10^{-3}$ atm, VI/II ratio = 0.55, Total flux = 0.5 l/min and T_{sub} = 395 ºC.

CONCLUSIONS

Numerical simulations of the deposition of CdTe in an in-line AP-MOCVD have been conducted using CFD code -Fluent. In these simulations, the influence of the process controlling parameters such as total flow rate, reactor pressure and substrate temperature on the deposition behaviour and the growth rate of the CdTe MOCVD in an in-line reactor with DIPTe and DMCd as precursors and H_2 as the carrier gas, has been assessed. The study has examined mass transport and kinetics regimes with the temperature ranging from 355 °C to 455 °C. The numerical results have been compared with the experimental data obtained from the measurement of the deposition, as conducted in an actual in-line MOCVD reactor. The numerical results are in general agreement with the experiments. The conclusions drawn from the present study are summarised as follows:

(1) For a given total gas flux with a constant molar flow of precursors from the inlet, the CdTe growth rate decreases as the total flux increases, and the uniformity of the growth rate along the substrate is remarkably improved.

(2) For a constant partial pressure of precursors, the CdTe growth rate are significantly influenced by the carrier gas flow field inside the reactor, implying the effect of reactor geometric conditions.

(3) For a given total flux and molar fraction of precursors (DIPTe and DMCd) introduced to the reactor, the CdTe growth rate is affected by the reactor pressure.

(4) The simulation results have clearly indicated the likely deposition covering area and growth thickness which may facilitate the control and optimisation of deposition process in the MOCVD.

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