Conference Paper

Numerical simulation and analytical models for thin film CdTe layers deposited by an inline AP-metalorganic chemical vapour deposition process

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This is a paper presented at the 12th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics

NUMERICAL SIMULATION AND ANALYTICAL MODELS FOR THIN FILM CDTE LAYERS DEPOSITED BY AN INLINE AP-MOCVD PROCESS

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ABSTRACT

The metalorganic chemical vapour deposition (MOCVD) as an attractive method for depositing CdTe and other group II-VI compound thin films has been widely used for fabrication of optoelectronic devices, including photovoltaic solar cells. The thin film deposition of CdTe layer on a substrate with dimethylcadmium (DMCd) and diisopropyltelluride (DIPTe) as precursors has been investigated both numerically and experimentally using an inline reactor. The present work mainly focuses on two aspects of the inline AP-MOCVD process: (1) effects of key deposition parameters such as the substrate temperature T_s, the deposition profile, the film thickness distribution and material utilisation on the pyrolysis of CdTe using the dynamic mode (moving substrate) in the simulation; (2) optimisation of the process conditions using static mode (stationary substrate). Both two-dimension (2D) and three-dimension (3D) computational fluid dynamics (CFD) modelling simulations were conducted to simulate the deposition process. Two modelling modes were trialled in the present work, one with the 2D simulation and optimisation of process conditions being conducted by adopting the dynamic mode and the other with 3D simulation but adopting the static mode. The use of dynamic mode in the CFD modelling for CdTe thin film MOCVD was found to be more suitable for approximation of the actual deposition process. The predicted thin film growth rates are consistent with those obtained from the deposition experiments.

INTRODUCTION

Cadmium telluride (CdTe) is one of the best recognised materials for fabrication of thin film solar cells [1] while the metalorganic chemical vapour deposition (MOCVD) which can be used for deposition of CdTe has attracted a lot of attention due to its advantages of producing high structural quality CdTe thin film layer over a large area substrate and its great commercial value [2]. Although MOCVD has become a relatively mature technology for CdTe thin film deposition and the existing capability of the process control has brought the MOCVD to a reliable thin film preparation [3], the mechanisms of the deposition of thin film CdTe layer by an in-line AP-MOCVD reactor process is still not well understood. The aim of this study is to apply CFD modelling to the simulation and optimisation of the deposition processes using the in-line AP-MOCVD process. Several previously reported studies using CFD modelling in the open literature have demonstrated that the MOCVD processes can be well predicted [4-7] because the use of CFD is not only adequate for prediction of the CdTe growth rates but also convenient for optimisation of the deposition process.

Two-dimensional (2D) numerical simulations for MOCVD processes based on CFD modelling approach were well documented in many previous studies. Kuhn *et al.* [8] applied the 2D simulation for the prediction of the deposition in a horizontal MOCVD reactor. Similarly, Tena-Zaera *et al.* [9] also used a 2D model in the simulation of CdTe deposition using a horizontal reactor by considering the coupling of heat transfer, mass transport and the species chemistry. However, these simulation results lack the support from the experimental validation. There are a few of studies based on three-dimensional (3D) CFD modelling for prediction of CdTe thin film deposition using MOCVD process. Liu *et al.* [10,11] and McDaniel *et al.* [12,13] employed the boundary-layer model coupling the kinetic of chemical reactions in a tubular reactor for prediction of the deposition rates. To date, the studies on the use of CFD modelling for prediction of the deposition and fluid dynamics behaviours in the MOCVD processes are still limited, especially when the surface chemical reaction chemistry is concerned. In contrast to the studies on CFD modelling of the CdTe MOCVD process, the researches focusing on the analysis of material performance and development of CdTe growth using the MOCVD technique through experiments have been reported [14-17]. It is necessary to explore the use of CFD modelling to simulate the real deposition process, in particular the modelling being extended to the three-dimension problems with considering the reaction chemistry.

In spite of the above mentioned studies on CdTe thin film growth, there are still many difficulties remaining in the practical simulations of the deposition process using CFD modelling approach. One big limitation is how to approximate and simplify the complicated multistep chemical reactions occurring on the substrate surface. For the CdTe deposition processes, there exist a significant inconsistency for the pre-exponential factor and the activation energy for description of

the involved chemical reactions when using the well-known Arrhenius equation. In order to better fit the experimental results, the parameters of kinetics of surface chemical reaction have to be modified. It has been generally accepted that the sequential reactions involved in the CdTe deposition process can be replaced by adopting a proposed global surface reaction in the CFD modelling as far as the major characteristics of the reactions can be reflected. The simplified global reaction assumed in the CFD modelling was reported in our previous study [19, 24].

The unavoidable numerical diffusion arising from the CFD modelling is strongly associated with the mesh size and mesh quality and this significantly affect the accuracy of the prediction of the deposition rate which is also influenced by the approximations introduced in the mathematical models, boundary conditions and the numerical discretisation scheme employed in the simulation. The aim of this study is to reveal the effect of mesh size and mesh qualities used in the CFD modelling on the prediction of the CdTe thin film deposition rates on a substrate by varying the temperature on the substrate surface. The CdTe thin film was deposited through the usage of an inline deposition process with a novel MOCVD reactor. Dimethylcadmium (DMCd) and diisopropyltelluride (DIPTe) were used as the precursors, injected from a showerhead into the reaction chamber. CFD modelling simulates the case where a substrate (75×50×3 mm^3) was placed in the reactor and was deposited. The simulations were run in two modes: dynamic and static modes [20, 21]. All simulations were conducted by using CFD code-ANSYS Fluent [22]. For improving the prediction to match the experimental data obtained from the real inline reactor process, the adoption of a sliding mesh for moving susceptor was proposed. To the best knowledge of the authors, there is no reported study on adopting this kind of model into the CFD modelling for prediction of CdTe thin film deposition process although this method has been widely used for stirred reactor simulations in mixing [23].

This paper is organised into three parts, description of the details of the modelling process, numerical modelling and discussion on simulation results and conclusions reached from the current study.

NOMENCLATURE

A	[s^{-1}]	Pre-exponential factor
c_p	[J/(kg·K)]	Heat capacity
$C_{precursor}$	[kg/m^3]	Concentration of precursor
D_i	[m^2/s]	Binary diffusion coefficient of species i
D_i^T	[m^2/s]	Thermal mass diffusion coefficient of species i
E_a	[kcal/mol]	Activation energy
$\boldsymbol{g}$	[m/s^2]	Gravity acceleration
GR	[μm/min]	Growth rate of surface reaction
H_i	[J/mol]	Enthalpy of species i
K	[-]	Number of chemical species
N	[-]	Number of chemical species
P	[pascal]	Operating pressure of reactor
$\boldsymbol{q}$	[J/m^2·s]	Heat flux vector
R	[J/(mol·K)]	Universal gas constant
R_r^f	[mol/(m·s)]	Rate of forward chemical reaction
R_r^b	[mol/(m·s)]	Rate of backward chemical reaction
R'	[-]	By-products of surface reaction
T	[K]	Temperature
T_s	[K]	Substrate temperature
$\boldsymbol{V}$	[m/s]	Velocity vector of gas flow
Y_i	[-]	Mass fraction of species i

Special characters

B	[-]	Unitless factor
Σ	[Å]	Collision diameter
ε/k	[K]	Characteristic potential
$\boldsymbol{T}$	[kg/m^3]	Density of the gas flow
$\mathcal{Z}$	[Pa]	Viscous stress tensor

Subscripts

AP	Atmospheric pressure
G	Gas
I	Species i
s	Solid

NUMERICAL MODEL DESCRIPTION

An in-line MOCVD reactor which was self-designed in CSER OpTic has been used as a referenced geometric model employed in the CFD simulations. The reactor details can be found in [20]. For the growth of CdTe layer, the DMCd and DIPTe are transported by carrier gas – hydrogen (H_2) and are introduced into reactor through the injection head. The entire MOCVD reactor is sealed by the nitrogen (N_2) - filled between the outside of the reactor and the system - to seal the tolerable gap between the outside walls from the inevitable manufactured errors; and also to cool the hot reactor despite the water cooling that is adopted. CdTe growth was deposited on the heated substrate with the size of 75×50 mm^2; the substrate can be set as stationary or moving according to the situations. The temperature of the substrate is assumed to be uniformly distributed, varying from 355 to 455 °C. The total flow rate is set to be 0.5 l/min with the II/VI ratio remaining at 0.55. An atmospheric pressure condition was assumed in the simulations.

A simplified geometric model based on the actual MOCVD reactor and the mesh imposed for the set-up is shown in Figure 1. The entire computational domain contains approximately 310,000 cells.

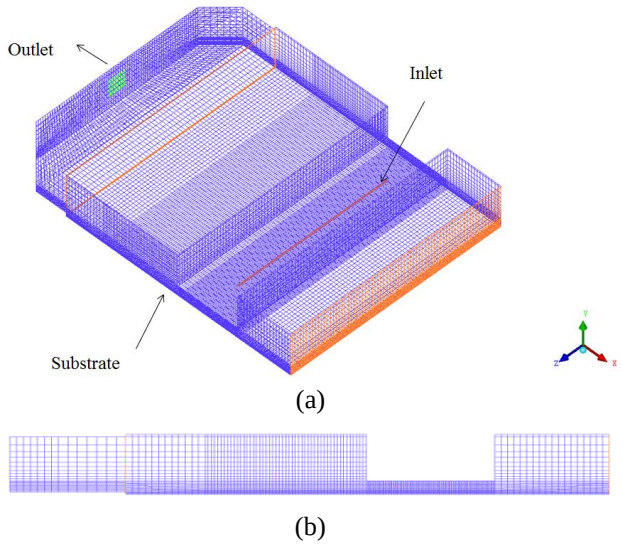

Figure 1 The mesh set-up used in CFD modelling: (a) 3D overview (b) the front view

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 imposed. To ensure that the skewness of the mesh is as small as possible, hexahedral structured cells were used throughout the computational domain. Considering the grid resolutions, the mesh size was chosen in such a way that the size is gradually refined towards the bottom wall of the reactor, reducing the numerical diffusion arising from the simulation.

On the other hand, the sliding mesh method was used for the 2D simplification model. Accordingly, the reactor is defined into two regions, consisting of the reactor chamber and the moving susceptor (Figure 2). The reactor chamber is kept to be stationary while the moving substrate slides along the bottom of the chamber by specifying an interface between the two mesh set-ups.

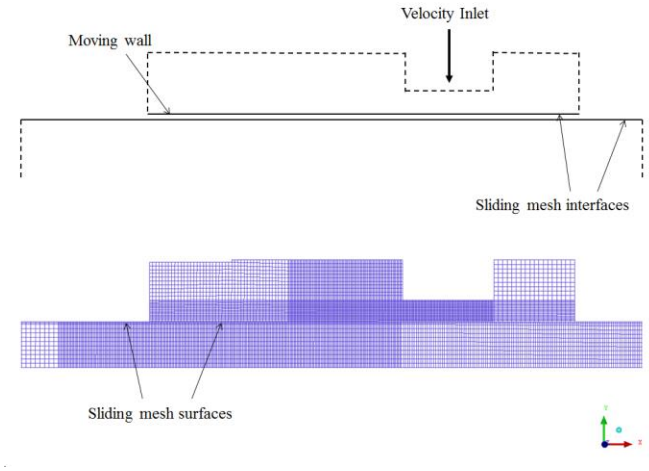

Figure 2 Treatment of the moving substrate and the mesh set-up (the sliding mesh)

The MOCVD is a complex process which involves various transport phenomena. In both numerical models, the flow in the reactor was assumed to be steady and the carrier gas was assumed to obey the ideal gas law. The Reynolds number based on the hydraulic diameter of the reactor falls into a range of 1 to 100, indicating that the gas flow in the reactor can be regarded as laminar flow. No-slip boundary condition was applied to the walls of the reactor. Steady state is considered for the static mode simulation, because the growth rate of thin film is very slow compared to the velocity of gases. However, for the dynamic mode simulation, time dependent simulation has been adopted to assess the effect of the deposit cumulated on the thin film thickness growth. The governing equations which describe the CdTe deposition process are listed in Table 1.

Table 1 Governing equations in the reactor

Name	Equations	
Conservation of mass	$\nabla \cdot (\rho \boldsymbol{v}) = 0$	(1)
Conservation of momentum	$\nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v}) + \nabla P = -[\nabla \cdot \boldsymbol{\tau}] + \rho \boldsymbol{g}$	(2)
Conservation of energy	$c_p \frac{\partial \rho T}{\partial t} + c_p \nabla \cdot (\rho \boldsymbol{v} T) = \nabla \cdot \boldsymbol{q} + \frac{DP}{Dt} - \boldsymbol{\tau} : \nabla \boldsymbol{v} - \sum_{i=1}^{N} \sum_{j=1}^{K} H_i \boldsymbol{v}_{ir} (R_r^f - R_r^b)$	(3)
Species transport	$\nabla \cdot (\rho \boldsymbol{v} Y_i) + \nabla \cdot (-\rho D_i \nabla Y_i - D_i^T \frac{\nabla T}{T}) + [\nabla \cdot \boldsymbol{\tau}] = R_i$	(4)

In addition, the reaction chemistry of the CdTe deposition involves multistep reactions but an overall surface reaction is assumed in the present study [24]:

$$(CH_3)_2Cd\ (g) + (C_3H_7)_2Te\ (g) \rightarrow CdTe\ (s) + R'\ (g)$$

where R′ indicates all the products and by-products which yielded from the surface reaction. The detailed mechanism has been simplified by assuming a rapid surface reaction in the simulation process. Since the carrier gas flow has been assumed as ideal gas flow, the mass diffusivities and thermal diffusivities of the gas mixture can be determined using the kinetic theory. The rate constant of the surface reaction can be expressed by the Arrhenius equation [25]:

$$k = AT^{\beta} \exp(-E_a/RT) \quad (5)$$

where A is the pre-exponential factor, T is the temperature, β is temperature index, E_a is the activation energy and R is the universal gas constant. Because the pre-exponential factor A and the activation energy E_a change significantly and there are not censors data available in the open literature, we have employed a set of data (assuming the combination of the two precursors in the overall surface reaction), obtained from fitting the experimental data.

RESULTS AND DISCUSSION

Static mode simulation

In order to evaluate the effect of substrate temperature on the CdTe growth rate, the substrate temperature was varied from 355 ºC to 455 °C, which covers two dominant regions, mass transport limited and kinetic limited. As can be seen from equation (5), kinetic limited process is significantly affected by the temperature. In the simulations, the activation energy has been estimated to be equal to 40 kcal/mol based on the fitting from the experimental data. II/VI ratio was kept to be equal to 0.55.

The grid sensitivity studies were first applied on two different grids in 2D model. To investigate the effect of grid size, the simulations were also conducted by employing the same operation conditions as the 2D model in 3D modelling case. The second order upwind differencing scheme and the SIMPLEC algorithm were used in the simulations. As can be seen from Figure 3, the predicted CdTe mass deposition rates when employing the hexahedral fine structured grid are in better agreement with the experimental ones than the use of the coarse mesh, indicating that the mesh set-up in modelling of the MOCVD has an impact on the prediction accuracy. This may

be explained by the fact that great changes in the velocity and temperature fields occur throughout the boundary layer in the neighbouring of the substrate surface. Any numerical diffusion arising from the simulations may cause errors. Thus, a refined mesh should be imposed in the vicinity of the substrate surface in order to capture the fluid dynamics and deposition behaviours. The relatively coarser mesh has been applied in the rest of the fluid domain except for the showerhead inlet region where the diffusion behaviour again affects the prediction of the flow and deposition behaviours. It seems that the deposition rate prediction in the kinetic limited regime is more sensitive to the mesh size than that in mass transport control regime. This can be seen from the equation (3) for energy conservation since the contribution from the term to account for the chemical reaction appearing in the equation is closely associated with the mesh size for numerical simulation. On the other hand, the mid-temperature range is limited by mass transfer and the effect of the mesh size on the predicted CdTe mass deposition rates is not remarkable.

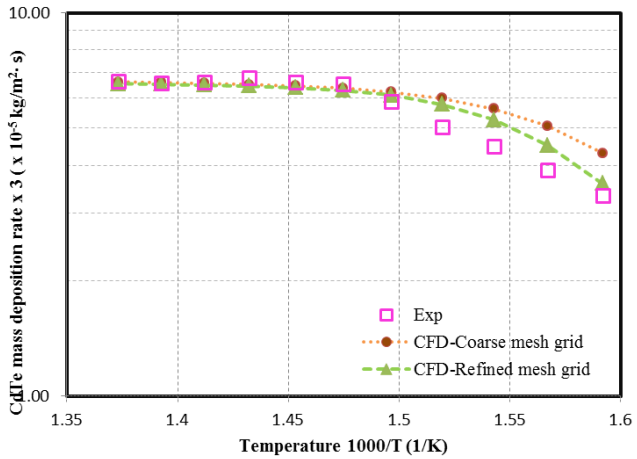

Figure 3 Predicted CdTe deposition rates versus the substrate temperature when using both the coarse and fined mesh in 3D modelling

Dynamic mode simulation

A trial study was conducted in a time-dependent two dimensional modelling of CdTe thin film deposition by using the sliding mesh method, coupled with the chemical kinetics. The simulation was performed by using a time step of 1s and the total time steps are set to be 420s to accord with the actual experiments conducted.

The variation of the velocity field inside the reactor due to the interactions between the sliding susceptor and the reactor chamber can been clearly seen from Figure 4. With the susceptor gradually moving through the region underneath the showerhead, the area of the substrate to be deposited increases, i.e. more surface areas are exposed to the flow of the gas mixture from the impinging jet of the shower head. The similar behaviour can be seen very obviously in Figure 5. With the heated susceptor moving, more surface area of the substrate contact the precursors, thus more products will deposit on the substrate surface. This can be explained by the decreased mass fraction of DIPTe in the reactor chamber. Due to the recirculated large vortex, which can be seen from Figure 4, the right-hand-side chamber almost has no precursor remains.

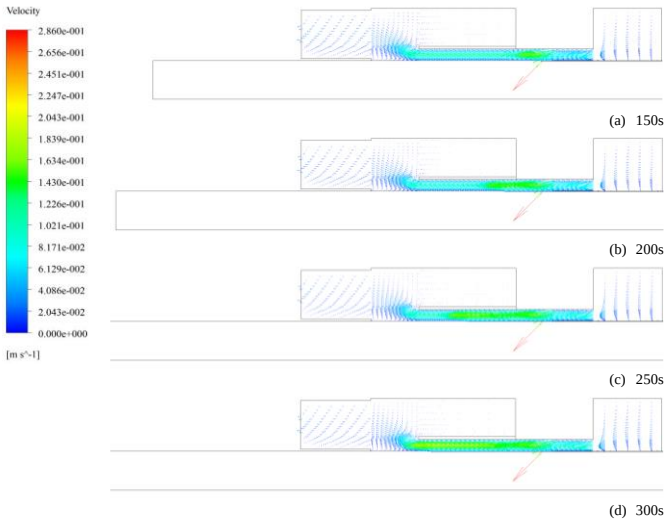

Figure 4 The velocity fields in the in-line AP-MOCVD reactor when using the sliding mesh model at times of (a) 150s, (b) 200s, (c) 250s and (d) 300s for the substrate surface temperature of 395 °C

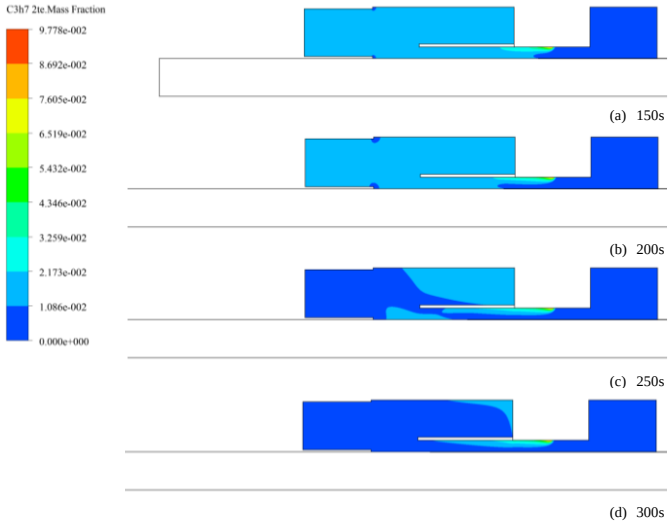

Figure 5 Contour of mass fraction of limiting species-$(C_3H_7)_2Te$ at the temperature of 395 °C at times of (a) 150s, (b) 200s, (c) 250s and (d) 300s

As a result, the growth rate of CdTe thin film layer with the time can be seen from Figure 6. The deposited CdTe is cumulated asymptomatically with the increase of the deposition time. When the deposition time is greater than 360s, the growth rate approaches a constant, likely caused by the balance of deposition and desorption of CdTe thin film layer on the substrate surface.

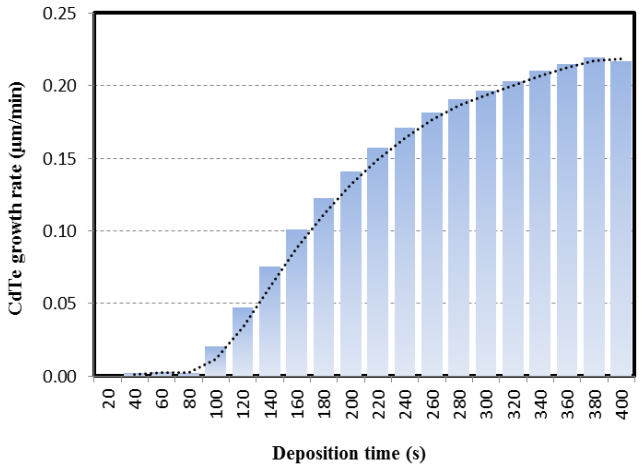

Figure 6 Time dependant variation of the CdTe growth rate predicted using the sliding mesh model

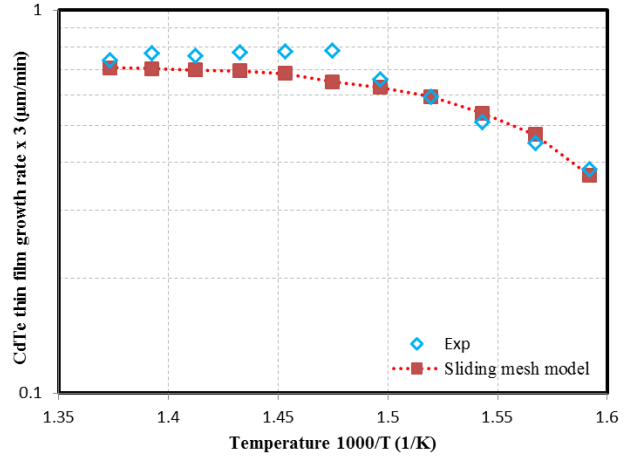

Figure 7 Comparisons between the CFD modelling on thin film growth rates and the experiment observations for different substrate temperatures.

Figure 7 shows the comparisons between the predicted thin film growth rates using the CFD modelling and the experimental data at different substrate temperatures. It can be seen from the figure that the simulated time dependent CdTe thin film growth rates are in a favourable agreement with the experimental ones. However, the CFD modelling results do not match up the experimental data in the region of the transition at the temperatures around 405 °C. This is likely caused by the under estimation of the diffusion coefficients D_i, because D_i is strongly depend on the species' properties, such as Lennard-Jones parameter which estimated based on kinetic theory [25], thus it is possible to be underestimation and this remains to be determined from the empirical correlations. Inaddition, D_i is also strongly affected by the temperature ($\propto T^{3/2}$). According to equation (4), both kinetic and mass transport terms affect the deposition rate. Also, based on equation (5), it is known that the kinetic term is proportional to exp (-1/*T*). Therefore, if the deposition process starts to be limited by mass transport at the temperature around 405 °C, numerical analysis results may not show a sudden change the same as the experimental results. Further study on this regard is required.

CONCLUSION

The results obtained using the time-dependent CFD modelling clearly indicates that the grid size and quality significantly affect the predicted CdTe thin film deposition rates, especially for the kinetic limited regime. The effect of the mesh size and quality has to be considered carefully in the CFD modelling of the MOCVD process.

The use of sliding mesh method has shown to be successful for simulation of CdTe thin film layer deposition in an inline MOCVD reactor. It has been demonstrated that the use of this method may capture the time-dependant deposition behaviour and reflect the effect of the moving substrate. Further testing and validation of this method may be necessary. The sliding mesh model may be valuable for optimisation of the deposition process, which may be used for the design of new MOCVD reactors.

ACKNOWLEDGEMENT

Yiyi Wu wishes to thank the financial support from the University of Nottingham Ningbo through an UNNC PhD scholarship. Thanks are also gone to the technical support from the research group in Centre of Solar Energy Research (CSER), OpTIC Glyndŵr, St Asaph Business Park, St Asaph, UK.

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