NUMERICAL SIMULATION OF POLYSILICON DEPOSITION CHARACTERISTICS IN CHEMICAL VAPOR DEPOSITION PROCESS

by

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This paper addresses the complex component evolution and silicon dynamic deposition characteristics in the traditional Siemens reactor. A two-dimensional heat and mass transfer model coupled with a detailed chemical reaction mechanism was developed. The distributions of temperature, velocity, and concentration are presented in detail. The influencing factors (such as feeding mole ratio, inlet velocity, base temperature and reactor pressure) on the molar concentration evolutions of ten major components and silicon growth rate were obtained and analyzed. Results show that base temperature is main influence of HCl mole fraction. In order to get more growth rate of silicon and better silicon quality, the complex operating parameters need to be reasonably designed on collaborative optimization.

Key words: *polycrystalline silicon, chemical vapor deposition,*
          deposition characteristics

Introduction

High-purity silicon continues to be of interest for the scientific community due to its potential in a wide range of novel applications as well as in basic research. Especially, high-purity silicon holds significant promise in integrated circuits and solar photovoltaic (PV) industry due to its high photoelectric conversion efficiency, low pollution, stable material properties, convenient industrial production and high-hole mobility [1]. Because of the dramatic rise of PV applications, the current production capacity of polysilicon increases rapidly [2, 3]. Large-scale production, high quality and low cost are the most important parameters for practical devices. As a solid silicon creator, the Siemens reactor consists of a chamber where several high-purity silicon slim rods are heated by electricity, and polysilicon is deposited on these seed rods at a high temperature about 1398 K [4]. A variety of by--products are generated in the deposition process, such as HCl, $SiCl_2$, SiH_2Cl_2, and so on. When the silicon rods take a long time with 60-80 hours for growing to a designed diameter, the silicon rods will be cooled down and removed off from the reactor [5]. These intricate situations result in limited conversions of the reactants and huge energy dissipation, especially

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when the heating is performed by electricity. Furthermore, the non-uniform surface temperature and reaction gas concentration are often blamed of heating a major reason for an inferior quality of the silicon products such as popcorn-like surface. Therefore, an in-depth understanding of the transport phenomena and chemical reactions in the reactor is of great significance for the optimization of Si CVD system.

While recent studies suggest that increasing energy utilization, selecting better reaction mechanism, enhancing the inner heat and mass transfer performance play crucial role in improving the Si CVD performance. Habuka [6] studied the chemical process of silicon epitaxial growth in SiHCl3-H2 system by numerical and experimental methods. Liu *et al*. [7] calculated the energy loss of CVD reactor with arbitrary distribution with any number of silicon using Monte Carlo ray tracing method and analyzed the effect of some parameters on radiative energy loss. Ni *et al*. [8] studied the multispecies thermal fluid transport and its interaction with the gas/surface reactions. Miao *et al*. [9] showed that high temperature, low pressure and low initial molar ratio of $SiHCl_3/H_2$ were favorable to the reduction reaction of $SiHCl_3$-H_2 system. But few studies show the detailed distributions of complex components in the CVD system, which calls for further study to improve the CVD performance.

In this article, we proposed a two-dimensional numerical model coupled with detailed gas/surface reactions for systemic research in Si CVD system. The results obtained by the model are in good with the experimental data from reference [6]. Diagrams of ten major components concentrations and silicon growth rate are presented and analyzed as a function of feeding mole ratio, inlet air velocity, reacting temperature and reacting pressure.

Model descriptions

Geometric model

The silicon deposition reaction carries out in a two-dimensional panel plates as illustrated in fig. 1. It consists of a surface, an inlet, an outlet and a wall in the model. The length of the deposition surface is 1.5 m and the width of the inlet and outlet is 0.1 m. The mixture of $SiHCl_3$ and H_2 enters the reactor at the left inlet. Then the gases react in the reactor and deposit the desired solid silicon on the surface of the substrate. Finally, the reactant and product leave the reactors through the right outlet.
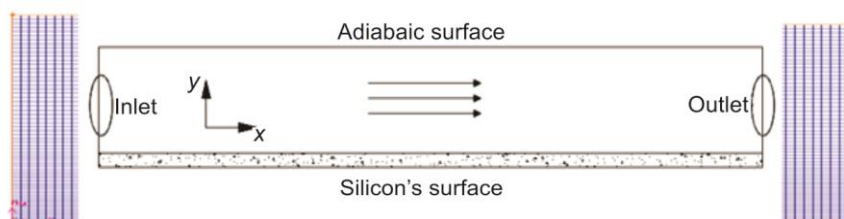

Figure 1. The geometric model of the deposition process

Governing equations and boundary conditions

The computational domain is shown in fig. 1. The flow direction is the x-direction and the radial direction is the y-direction. The boundary surface in the top of the model is set to be adiabatic, where neither mass nor heat can pass through. The deposition surface is defined as a constant temperature. The governing equations for continuity, momentum, energy and species in the computational domain are expressed:

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−   continuity equation:

$$\frac{\partial}{\partial x_i}(\rho u_i) = 0 \tag{1}$$

where u_i is the velocity in the i direction and fluid density ρ is expressed:

$$\rho = 1 / \sum_i{}' \left(\frac{m_i'}{\rho_i'} \right) \tag{2}$$

−   momentum equation:

$$\frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i + F_i \tag{3}$$

−   energy equation:

$$\frac{\partial}{\partial x_i}\left[u_i(\rho E + p) \right] = \frac{\partial}{\partial x_i}\left(k_{\text{eff}} \frac{\partial T}{\partial x_i} \right) - \sum_j h_{j'} J_{j'} + u_j(\tau_{ij})_{\text{eff}} + S_h \tag{4}$$

where k_{eff} is the effective thermal conductivity coefficient (including the molecular and turbulent thermal conductivity). The effect of heat transfer by radiation on the substrate temperature is ignored. The $J_{j'}$ is the diffusion flux of component j' expressed as eq. (5). The S_h describes the consumption and production of heat due to the chemical reactions.

Species transport equation:

$$\nabla(\rho v Y_i) = -\nabla J_i + R_i + S_i \tag{5}$$

$$R_i = M_i \sum_{i=1}^{N} R_{ir} \tag{6}$$

where R_i is the net rate of production of species i by chemical reaction, M_i − the molecular weight of species i, and R_{ir} − the Arrhenius molar rate of reaction/destruction of species i in reaction r.

Chemical reaction mechanisms and numerical approach

The detailed chemical reaction mechanism based on Ho's detailed [10] gas phase reaction and a set of semi-empirical surface reactions have been taken into account to study the silicon dynamic deposition characteristics. The equations of reactions and the kinetic parameters of $SiHCl_3$ and H_2 are shown in Ho's research [10], which are omitted herein for simplify.

The preprocessor GAMBIT 2.4.6 is used to generate the computational meshes. The final adopted grid number is 45000, which considered independent of grid size. The present simulation is performed using the FLUENT CFD program, combined with CHEMKIN, which offers detailed chemical reaction mechanism to FLUENT. A numerical scheme called SIMPLE with k-ε model is used to solve the governing equations. The reaction model is the eddy-dissipation concept (EDC) model which is an extension of the eddy-dissipation model including detailed chemical mechanisms in turbulent flows.

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The model and all reaction kinetics were validated using the experimental data published in the literature [6] from a single wafer CVD reactor. Referring to Habuka's research, silicon depositions took place in a horizontal reactor. According to the comparison of the experimental and numerical data, the deposition rate of silicon shows that the simulated result agrees well with the experimental values in literature [6]. So, our model can accurately describe the polycrystalline CVD process.

Results and discussion

Distribution of silicon deposition rate

Figure 2 presents the evolution of silicon deposition rate with curvilinear co-ordinate of the gas flow channel. It is observed that the silicon deposition rate exhibits a significant reduction in the entrance region of the channel with the maximum deposition rate of 16.8 μm/min. However, the deposition rate subsequently exhibits a slow decrease and asymptotically approaches a value of 4.9 μm/min. The result is due to the presence of larger $SiHCl_3$ concentration near the entrance. The $SiHCl_3$ concentration decreases gradually along the flow direction with the sustained consumption of reactants.
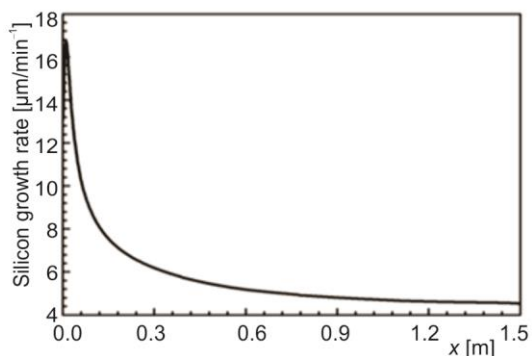

Figure 2. Evolution of silicon deposition rate with curvilinear co-ordinate

Distributions of temperature, velocity, and concentration

Figure 3(a) shows the temperature distributions in the straight gas flow channel. The temperature gradually decreases along the radial direction, which forcing the chemical vapor deposition reactions to occur at a distance of 0.01 m from the substrate surface. Figure 3(b) presents the velocity distributions in the channel. The change of velocity near substrate surface is obvious. In addition, the continuous deposition of solid silicon leads to sustaining increase of velocity along the axial direction.
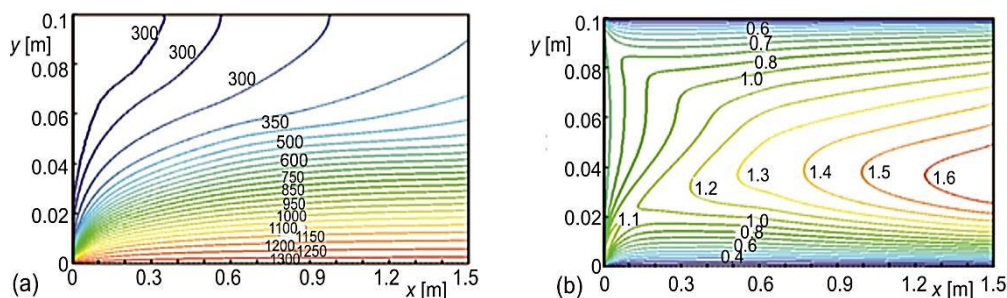

**Figure 3. The temperature and velocity distribution in 2-D reactor;
(a) temperature field, (b) velocity field**

A variety of by-products are generated in the complex polycrystalline silicon CVD process, for example, HCl, $SiCl_2$, SiH_2Cl_2, $SiHCl$, $SiCl_4$, SiH_2, $Si_2H_2Cl_4$, Si_2HCl_5, Si_2Cl_6. The concentration distributions are illustrated in fig. 4. It can be seen that the distribution rules of

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reactants H_2 and $SiHCl_3$ are similar from fig. 4 (a) and (b). Owing to the continuous consumption of reactant, the concentrations of reactants decrease along the negative direction of y axis and flow direction. In fig. 4(c), the concentration of HCl increases continuously along y axis, revealing that HCl is absorbed onto the substrate surface to continue participating in the deposition reaction. But HCl can etch substrate surface, affecting the yield and quality of silicon. Fig. 4 (d) presents the concentration distribution of Si_2HCl_5, leaving the boundary layer and flowing out of the reactor with main air-flow.
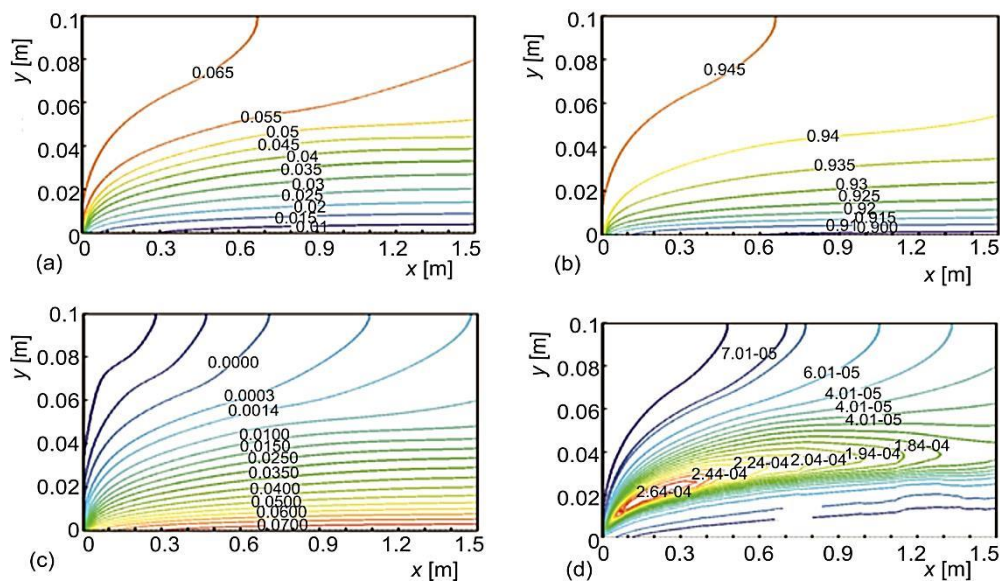

Figure 4. Mole fraction distributions of components; (a) $SiHCl_3$, (b) H_2, (c) HCl, (d) Si_2HCl_5

Effect of operating parameters on the component molar fraction distribution

Figure 5(a) presents molar fraction evolutions for ten major components with the inlet mole fraction of H_2 at the temperature of 1398 K, pressure of 1 atmosphere and inlet velocity of 0.67 m/s. For the gas components except H_2, a significant reduction in the components mole fraction is observed by a factor of the weakening of chemical reactions. It is due to the reduction of reactant $SiHCl_3$ ratio induced by the increase of the H_2 mole fraction, and hence, the silicon production reduces. So, a reasonable H_2 concentration can cause high silicon CVD reaction efficiency.

Figure 5(b) presents molar fraction evolutions for ten major components with the inlet velocity at the temperature of 1398 K, pressure of 1 atmosphere and the H_2 mole fraction of 0.945. It can be seen that the increasing inlet velocity brings monotonic rise in mole fraction of H_2 and $SiHCl_3$ and decline in other byproducts. Under low inlet velocity, mass transport is the main control factor of silicon deposition rate, the more adequate gas phase reactions results in higher byproduct concentrations. Under high inlet velocity, the thinning boundary layer enhances chemical reactions, increasing the silicon deposition rate. However, higher inlet velocity generates a large amount of excess gases. The result is that the mole fraction of the byproducts decreases and the reaction gases are not fully utilized.
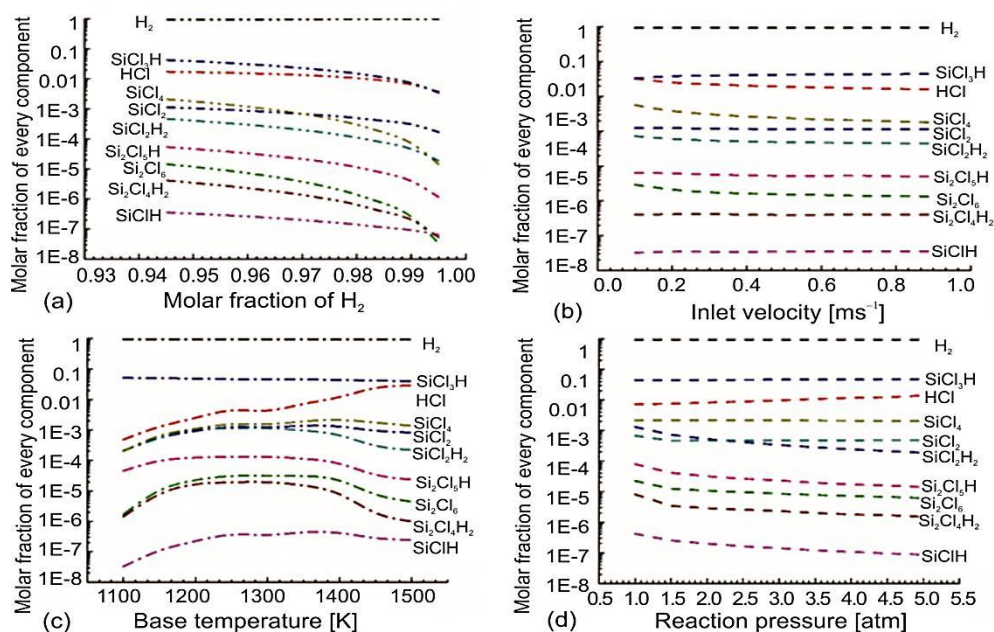
Figure 5. The molar fraction evolutions of every component with; (a) molar fraction of H₂, (b) inlet velocity, (c) base temperature, (d) reaction pressure

Figure 5(c) reveals the molar fraction evolutions of ten major components with the base temperature at the inlet velocity of 0.67 m/s, pressure of 1 atmosphere and H_2 mole fraction of 0.945. It can be observed that the mole fractions of $SiHCl_3$ and H_2 decrease with the temperature rising, because the deposition reactions of silicon are endothermic reaction. The concentration distributions of other by-products present three different variation laws. From 1100 K to 1200 K, the mole fractions of all by-products increase with the temperature rising. When the temperature continues to increase to 1400 K, the mole fractions of most by-products remained essentially constant. From 1400 K to 1500 K, each component shows different variation tendency. With the huge increase of mole fraction of HCl, the mole fractions of SiH_2Cl_2, $SiHCl_5$, Si_2Cl_6, and $Si_2H_2Cl_4$ gradually decrease, and the mole fractions of $SiCl_4$, $SiCl_2$, and $SiHCl$ remain essentially unchanged. Because the high concentration of gas HCl can erode the substrate surface and affect the silicon quality, the temperature need to be controlled around 1400K.

Figure 5(d) shows the mole fraction evolutions of ten major gas phase components with reaction pressure at the inlet velocity of 0.67 m/s, base temperature of 1398 K and H_2 mole fraction of 0.945. As the pressure rises from 1 to 5 atm, the mole fractions for $SiHCl_3$ and H_2 increase slowly, while for other byproducts change little. The increase of mole fraction of HCl is tiny comparing to the influence of the temperature on it. The small increase of mole fractions in $SiHCl_3$ and H_2 implies a little reduction in the degree of reactions. The result is due to that the total coefficient of the products is larger than that of the reactants and the increasing pressure inhibits the forward reactions.

Effect of operating parameters on the silicon deposition characteristics

Figure 6(a) shows the effect of inlet hydrogen mole fraction on the growth rate of silicon at the temperature of 1398 K, pressure of 1 atm and inlet velocity of 0.67 m/s. The Si

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growth rate exhibits a classical power law increase and approaches the maximum value of 9.8 μm min^{-1} at the H_2 mole fraction of 0.8. The result is due to that the increasing H_2 mole fraction creates more crash chances for $SiHCl_3$ and H_2 so as to improve the $SiHCl_3$ conversion rate. The sustained increase of H_2 mole fraction leads to continuous reduction in $SiHCl_3$ mole fraction, which reduces the Si deposition rate and the effective utilization of H_2. But, actually, the high mole fraction of H_2 is helpful to deoxidize $SiHCl_3$ to polysilicon as much as possible and decrease the difficulty of separating $SiHCl_3$ and H_2 form reaction product. In the real reactor, the H_2 mole fraction in the vicinity of 0.9 is always selected for reaching a balance between Si growth rate and $SiHCl_3$ conversion rate.

Figure 6(b) shows the effect of inlet velocity on the growth rate of silicon at 1398 K, 1 atmosphere, and inlet H_2 mole fraction of 0.945. It is apparent that the Si growth rate exhibits a sustained growth and asymptotically tends to be stable. Although, the increscent inlet velocity offers sufficient reactants increasing the Si growth rate, but contemporaneously reduces the reactants conversion ratio. Otherwise, high inlet velocity will enhance heat transfer process and result in high energy consumption. So, appropriate inlet velocity is requisite to the cost reduction.
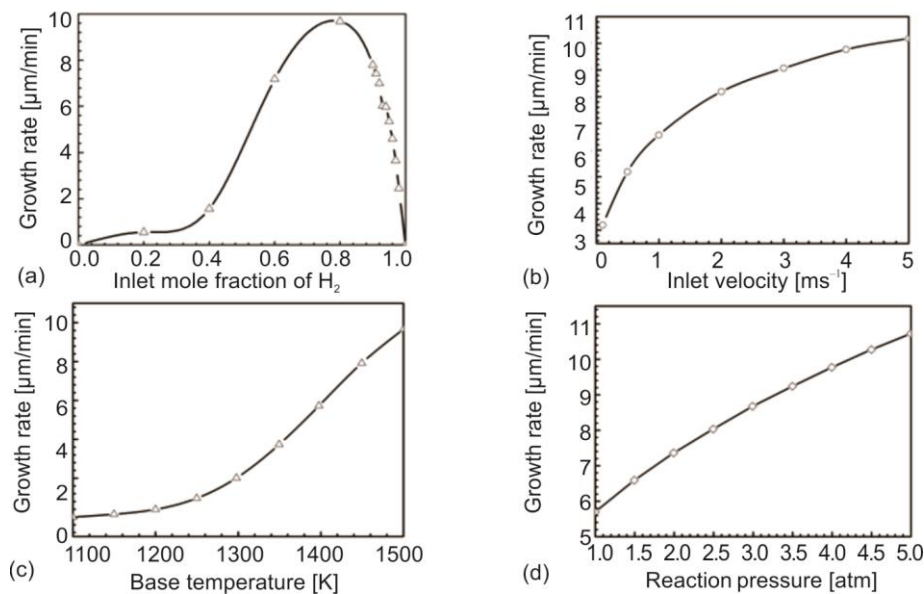

Figure 6. Effect on growth rate of silicon from the parameters of;
(a) molar fraction of H2, (b) inlet velocity, (c) base temperature, (d) reaction pressure

Figure 6(c) shows the influence of reaction temperature on the Si growth rate at 1 atmosphere, inlet velocity of 0.67 m/s and inlet H_2 mole fraction of 0.945. It can be observed that the Si growth rate first slowly increase to 2.02 μm per minute at 1300 K, then exhibits a classical power law increase. The rule is dominated by endothermic Si CVD deposition reactions. In addition, high temperature brings better crystalline properties and metallic luster on silicon surface. Nevertheless, higher temperature adds more loads to the equipment, enhances corrosion reactions and brings more impurities. In the real furnace, the temperature ranging from 1327~1427 K is appropriate for the Si deposition process when Si growth rate and silicon quality need to be synthetically considered.

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Figure 6(d) shows the influence of reaction pressure on the Si growth rate at 1398 K, the inlet velocity of 0.67 m/s and the inlet H_2 mole fraction of 0.945. It is apparent that the Si growth rate increases linearly with the pressure rising in the reactor. It implies the enhancement of degree for Si deposition reactions, namely, more crash chances among reactants. It is due to that the elevated pressure brings increase for the reactants concentration. However, the operation of the reactor under higher pressure and high temperature will increase the difficulty of solving thermal stress problems. In order to avoid mechanical damage and ensure the safety of the CVD system, the pressure ranging from 0.3~0.4 MPa is conductive to Si deposition process in actual reduction furnace.

Conclusions

In this paper, a 2-D heat and mass transfer model coupled with gas reactions and surface reactions was carried out to simulate the deposition characteristics of silicon in a trichlorosilane and hydrogen system. Compared with the experimental results, the model is validated. The distributions of the multi-component concentration and growth rate of silicon affected by the inlet H_2 mole fraction, inlet velocity, base temperature and reaction pressure are obtained and analyzed in detailed.

The results show that a large temperature gradient exists in the reactor and the chemical vapor deposition reaction occurs in the boundary layer. The distribution patterns of ten main gases in the reactor containing H_2, $SiHCl_3$, HCl, $SiCl_2$, SiH_2Cl_2, $SiCl_4$, Si_2HCl_5, Si_2Cl_6, $Si_2H_2Cl_4$, and $SiHCl$ are different because the velocity and the concentration of the fluid are largely influenced by chemical reactions. The influence of base temperature on mole fraction of HCl is more than that of other parameters. In order to get more growth rate of silicon and better silicon quality, the complex operating parameters need to be reasonably designed for different optimization target. Furthermore, the suggesting parameters are provided.

Acknowledgment

Nomenclature

E	– reaction activation energy, [cal/mol]	T	– absolute temperature, [K]
h	– convective heat transfer coefficient, [$Wm^{-2}K^{-1}$]	u	– fluid velocity, [ms^{-1}]
		Y	– molar concentration [$molm^{-3}$]
Jj'	– diffusion flux of component j', [–]	x, y	– co-ordinate system, [–]
k_{eff}	– effective thermal conductivity coefficient, [$Wm^{-1}K^{-1}$]	*Greek symbols*	
L	– characteristic length, [m]	ρ	– fluid density, [kgm^{-3}]
M	– molecular weight, [–]	τ	– tangential force, [Nm^{-2}]
P	– pressure, [atm]		
R_i	– net rate of production of species i by chemical reaction, [–]	*Acronyms*	
		CVD	– chemical vapor deposition, [–]
R_{ir}	– Arrhenius molar rate of reaction/destruction of species i in reaction r, [–]	EDC	– eddy-dissipation concept, [–]
		PV	– photovoltaic
		TCS	– trichlorosilane, [–]
Q_w	– heat flux [wg^{-1}]		
S_h	– consumption and production of heat due to the chemical reactions, [–]		

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