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Modeling chemical vapor deposition of silicon dioxide in microreactors at atmospheric pressure

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Abstract. We developed a multiphysics mathematical model for simulation of silicon dioxide Chemical Vapor Deposition (CVD) from tetraethyl orthosilicate (TEOS) and oxygen mixture in a microreactor at atmospheric pressure. Microfluidics is a promising technology with numerous applications in chemical synthesis due to its high heat and mass transfer efficiency and well-controlled flow parameters. Experimental studies of CVD microreactor technology are slow and expensive. Analytical solution of the governing equations is impossible due to the complexity of intertwined non-linear physical and chemical processes. Computer simulation is the most effective tool for design and optimization of microreactors. Our computational fluid dynamics model employs mass, momentum and energy balance equations for a laminar transient flow of a chemically reacting gas mixture at low Reynolds number. Simulation results show the influence of microreactor configuration and process parameters on SiO₂ deposition rate and uniformity. We simulated three microreactors with the central channel diameter of 5, 10, 20 micrometers, varying gas flow rate in the range of 5-100 microliters per hour and temperature in the range of 300-800 °C. For each microchannel diameter we found an optimal set of process parameters providing the best quality of deposited material. The model will be used for optimization of the microreactor configuration and technological parameters to facilitate the experimental stage of this research.

1. Introduction and microreactor design

Microreactor technology as part of microfluidics offers many advantages compared to the macroreactors: high efficiency of heat and mass transfer, precise control of process parameters and easy migration from lab experiments to commercial production. Synthesis of nanomaterials with unique properties is the most interesting application of microreactors, for instance monodisperse nanoparticle production from liquid phase [1, 2] or nanowires and nanorods deposition in a channel of microfluidic chip [3]. A relatively new direction in microreactor technology is Chemical Vapor Deposition (CVD), a popular method for nanomaterial manufacturing. In this paper we investigate the problem of microreactor CVD technology for silicon dioxide (SiO₂) deposition. We present a mathematical model and computer simulation results.

Silicon dioxide can be deposited from different chemical mixtures: silane with oxygen, dichlorosilane with oxygen, or TetraEthyl OrthoSilicate (TEOS). These mixtures differ in technological process conditions and quality of deposited materials. TEOS offers several advantages, most notably: (1) thermal decomposition can be operated at atmospheric pressure and (2) silicon atom in TEOS is in the same chemical state as in the deposited SiO₂, therefore it is not necessary to oxidize



it, which is beneficial from the chemical point of view. Oxygen is however added to avoid contamination of silicon dioxide with carbon, since oxygen reacts with the products of TEOS pyrolysis. Ozone is often used for reducing the temperature of TEOS decomposition [4, 5], but it is difficult to supply ozone in microreactors because of its high reactivity. Without ozone, production of silicon dioxide from TEOS is efficient at 700-900°C.

Our design of a microreactor is based on a macroreactor scheme [6]. The microreactor has two channels for gas supply: central channel for TEOS+Argon mixture and lateral ring channel for oxygen (see Figure 1). Argon was used as a carrier gas diluting TEOS. Varying the ratio between TEOS and O₂ flow rates, we can regulate the distribution of gas flow, deposition rate and localization. The goal of technology optimization is maximizing the deposition rate and TEOS utilization and minimizing the deposition area.

We simulated this CVD microreactor with three different diameters of the central channel: $d = 5, 10$ and $20 \mu\text{m}$. For each microchannel diameter we found an optimal set of process parameters providing the best deposition localization.

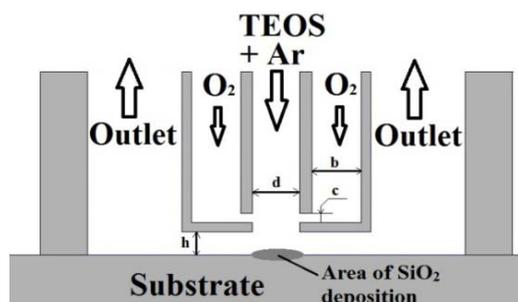


Figure 1. Microreactor scheme. $h=10 \mu\text{m}$; $b=20 \mu\text{m}$; $c=5 \mu\text{m}$; $d=5, 10, 20 \mu\text{m}$. Outlet ring width is $50 \mu\text{m}$.

2. Mathematical model and chemical reactions

Based on the calculated Knudsen numbers 10^{-3} – 10^{-2} , we selected a continuum modeling approach. In this range, slip boundary conditions for velocity and thermal jump on reactor walls shall be applied [7]. In the next stage of our research we will investigate the effect of these boundary conditions. Our mathematical model is based on mass, momentum and energy balance equations for a laminar transient flow of a chemically reacting gas mixture at low Reynolds numbers [8]. A model of chemical reactions is based on [9, 10]. The rate of a chemical reaction between species A and B is defined by

$$R = k \cdot [A] \cdot [B], \quad (1)$$

where $[A]$ and $[B]$ are the species concentrations, k is the reaction rate constant. The constants depend on temperature, as described by Arrhenius' equation

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

where A is a pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the temperature. Chemical reactions in the gas phase and on the surface selected for our model are presented in Tables 1 and 2. Silicon substrate with SiO₂ and adsorbed –OH groups is modeled as SiG₃OH. This surface specie reacts with the gas phase species, leading to SiO₂ deposition.

It is important to note that to obtain a better localization of silicon dioxide it is necessary to use a diffusion-limited regime, where diffusion of reactants is the slowest stage in reaction mechanism [11]. In this case the uncertainty in reaction rate values is not critical for the accuracy of simulation.

Table 1. Gas phase reactions

N	Reaction	A, cm ³ s ⁻¹	E _a , kcal/mol
1	SiE ₄ => Si(OH)E ₃ + C ₂ H ₄	4.9 · 10 ¹³	61.46
2	SiE ₄ + H ₂ O => Si(OH)E ₃ + C ₂ H ₆ O	1.0 · 10 ¹¹	25.00
3	Si(OH)E ₃ + SiE ₄ => O(SiE ₃) ₂ + C ₂ H ₆ O	1.0 · 10 ¹¹	30.00
4	2Si(OH)E ₃ => O(SiE ₃) ₂ + H ₂ O	1.0 · 10 ¹¹	30.00
5	C ₂ H ₅ OH => C ₂ H ₄ + H ₂ O	4.9 · 10 ¹⁴	65.50
6	C ₂ H ₄ + 3O ₂ => 2CO ₂ + 2H ₂ O	4.2 · 10 ¹³	60.80

"E" is the ethoxy group (OC₂H₅);

"G" denotes a "glass" Si-O bond, contributing 1/2 of the O atom to the Si atom

Table 2. Surface reactions

N	Reaction	A, cm ³ s ⁻¹	E _a , kcal/mol
1	SiGE ₃ => SiG(OH)E ₂ + C ₂ H ₄	5.1 · 10 ¹²	47.00
2	SiE ₄ + SiG ₃ (OH) => SiO ₂ + SiGE ₃ + C ₂ H ₆ O	8.8 · 10 ^{3*}	43.80
3	SiG(OH) ₂ E => SiG ₃ (OH) + C ₂ H ₆ O	2.2 · 10 ¹²	44.00
4	Si(OH)E ₃ + SiG ₃ (OH) => SiO ₂ + SiGE ₃ + H ₂ O	20.0*	12.00
5	SiG(OH) ₂ E => SiG(OH) ₂ E + C ₂ H ₄	3.4 · 10 ¹²	47.00
6	SiG(OH) ₂ E => SiG ₃ E + C ₂ H ₆ O	2.2 · 10 ¹²	44.00
7	SiG(OH) ₂ E => SiG ₃ E + H ₂ O	2.2 · 10 ¹²	44.00
8	SiG ₃ E => SiG ₃ (OH) + C ₂ H ₄	1.7 · 10 ¹²	47.00

* - sticking coefficient was used to simulate SiO₂ adsorption

3. Results and discussion

We have studied the influence of source gases flow rates and microreactor central channel diameter on the deposition rate and localization. Due to the page limit, here we show only the results for 800°C temperature, atmospheric pressure, 10 μm central channel diameter, and 1 sccm of TEOS+Ar mixture (0.15 sccm of TEOS and 0.85 sccm of Argon).

To illustrate the influence of source gases flow rates, we present velocity distributions for three TEOS-to-Oxygen ratios (Fig. 2). With 1 sccm of TEOS+Ar fixed, case “a” had 0.01 sccm of oxygen, case “b” 1 sccm, and case “c” 5 sccm of O_2 . Figure 3 shows Si(OH)E_3 distribution, the main product of TEOS decomposition, for the same three regimes (a,b,c).

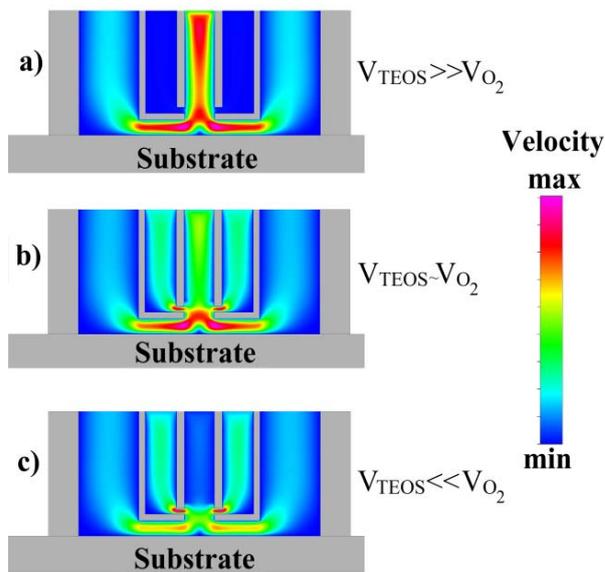


Figure 2. Gas velocity in microreactor. Three gas flow regimes: a) $V_{\text{TEOS}} \gg V_{\text{O}_2}$ b) $V_{\text{TEOS}} \sim V_{\text{O}_2}$ c) $V_{\text{TEOS}} \ll V_{\text{O}_2}$.

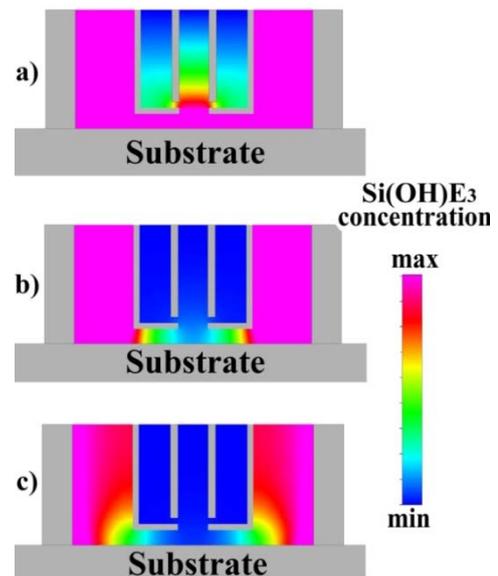


Figure 3. Distribution of Si(OH)E_3 concentration in microreactor

We observed that an increase of the oxygen flow (coming out of the ring near the substrate) confines the TEOS flow towards the central line of microreactor, thus the deposition area is reduced (see also Fig. 4). This is beneficial for the technology. But further increase in the oxygen flow reduces the rate of SiO_2 deposition, while we need to maximize it. Simulations will allow to find the balance between these two opposite trends, optimizing the process of micro-electro-mechanical systems (MEMS) production. Future work shall include studying also the influence of oxygen outflow direction and distance to the substrate.

For different diameters of the central TEOS channel or lateral O_2 ring channel, we can expect the same behavior, just at different values of the flow rates. We found the optimal TEOS: O_2 flow rate ratios for three diameters of the central channel, 1:55 for 5 μm channel; 1:100 for 10 μm channel; and 1:200 for 20 μm channel. It is important to note that the main factor in deposition localization is the ratio of flow velocities, rather than the total flow rates. It means that by varying the width of the oxygen channel we can control the flow streamlines, and thus the deposition area. Further study shall investigate the properties of the deposited SiO_2 , minimizing its contamination with carbon.

Figure 4 shows the deposition rate distribution along the substrate for cases “a” and “b” at diameter $d=10 \mu\text{m}$. In case “c” deposition is extremely low, thus it is not plotted in this figure. The Full Width Half Maximum (FWHM) of deposition in case “b” (at higher oxygen flow rate) is 8 μm , smaller than in case “a”, which is 12 μm . Case “b” represents a very good result, with the deposition width even smaller than the central channel diameter. Similar results were obtained in microreactors with central channel diameters of 5 and 20 μm .

Temperature dependence was investigated in the range from 300°C to 800°C (results are available in an extended report). For temperatures below 600°C the SiO₂ deposition stops, because TEOS thermal decomposition requires higher temperatures.

4. Conclusions and future plans

We developed a multiphysics mathematical model for simulation of silicon dioxide chemical vapor deposition from tetraethyl orthosilicate and oxygen mixture in a microreactor at atmospheric pressure. Several series of computational experiments have investigated the influence of TEOS to Oxygen flow rate ratios, process temperature and central channel diameter on deposition rate and

localization. Simulation results demonstrated three regimes of gas flows in microreactors. For each microreactor we found the TEOS/O₂ ratios separating these three regimes, and an optimum combination of process parameters, minimizing deposition area and maximizing deposition rate.

As the next step of this project, we will further adjust and validate the model. It includes studying the effect of velocity slip and thermal jump boundary conditions; investigating the influence of oxygen outflow direction and distance to the substrate; and optimizing the properties of the deposited material. For model validation, laboratory experiments will be carried out based on the preliminary results obtained in this work. The validated model will be used for designing microreactors for MEMS production technology.

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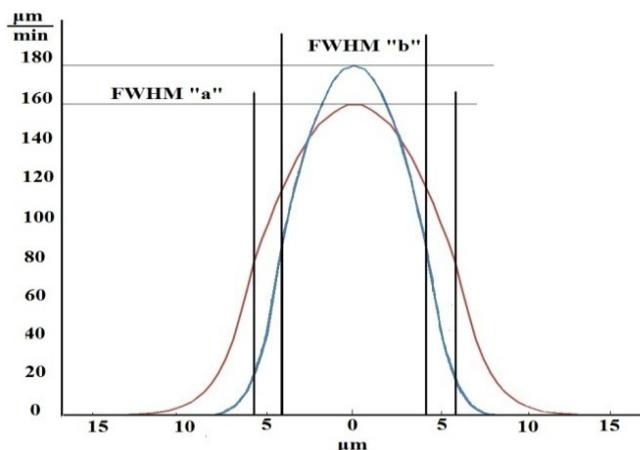


Figure 4. Distribution of deposition rate along the substrate for CVD microreactor with 10 μm central channel. Full Width Half Maximum (FWHM) for case “a” is 12 μm, for case “b” is 8 μm.