

Mathematical modeling of a heating system for a SnO₂ CVD reactor and computational fluid dynamics simulations (3D-CFD)

Dino Novosel
Faculty of Mechanical Engineering and Naval Architecture
University of Zagreb, Zagreb, Croatia
e-mail: Dino.Novosel@fsb.hr

Profa. Dra. Alaide Pellegrini Mammana
Coordenadora da Mostradores de Informação do CenPRA
Centro de Pesquisas Renato Archer
Rodovia D. Pedro I, km 143.6 — CEP 13082-120 Campinas, São Paulo, Brazil
e-mail: Alaide.Mammana@cenpra.gov.br

Željko Tuković
Faculty of Mechanical Engineering and Naval Architecture
University of Zagreb, Zagreb, Croatia
e-mail: Zeljko.Tukovic@fsb.hr

ABSTRACT

Study of the heat transfer of a continuous system that is being designed for the deposition of tin oxide thin SnO₂ films on soda-lime glass substrates of large dimensions (400 mm x 400 mm x 2 mm). This system will operate with infra-red heating (parallel mounted ceramics IR lamps in one unit) and will substitute the present CVD system, which is used in the CenPRA display pilot plant to coat substrates up to 150 mm x 150 mm x 2mm. In this system the substrates are heated by thermal conduction and the deposition is done by an "in house" process called vapor decomposition process (VDP). Assuming that the heat flow is an unique flux between two flat and parallel surfaces, the temperature as a time depended function can be calculated by equation as:

$$T = \frac{\sigma}{\rho \delta c \left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1 \right)} \int_{t_1=0}^{t_2=t_1} (T_1^4 - T^4) dt$$

By solving the equation using MatLab package, Simulink, obtained was logarithmic behavior of the temperature, and determined 23s as a necessary time to heat up soda-lime glass substrates of 2 mm thickness at 400° C if the heat source covers all the substrate area.

Using numerical solver FLUENT, simulated was VDP process at atmospheric pressure, taking in mind that the system consists of two parallelepiped-like chambers: the furnace containing the IR lamps in which the glass is heated, and the chamber where the deposition occurs. FLUENT helps us to obtain the resolution of the elementary differential equations for mass diffusivity, full multi-component thermal diffusion effects and reactions on the heated substrate.

The simulations permitted to get a 3D perspective of the deposited layer along the substrate surface and also to calculate the VDP process parameters as temperature, pressure, reaction rate for each species (O₂, Cl and HCl) and gas speed along the chamber.

Introduction

Brazil, the land of an internal sun! How to help the Brazilian population to increase energy efficiency by decreasing heat load of household air condition systems? The answer is *INTELLIGENT WINDOWS* and it was given by CenPRA

The CenPRA (Centro de Pesquisas Renato Archer) is an acronym for the major federal researching institute for microelectronics located in Campinas, Sao Paulo, Brazil. It is sponsored mainly from a government budget and therefore very often seeks the money for the investments of the necessary researching equipment. By help of young students they try to invent and design all necessary stuffs for the experiments.

During my 7th months stay in CenPRA on internship, I was enrolled into department for developing equipment and process improvement of the Liquid Crystal Displays.

There was existing old equipment for step-by-step producing of semi-conductive thin layers of SnO₂ on glass surfaces obtained with Chemical Vapor Deposition (CVD) of the gasses (SnCl₄, H₂O). Furthermore, those glasses were mounted into 'sandwiches' due to obtain semi-conductive polarized transparent layers. Connecting on those deposited glasses a microcontroller we will obtain intelligent window which will be used for reducing of income sun beams through the windows into houses.

Topic of the project was to invent, design and realize the new plant for continuously producing (substrate placed on moving belt which will first pass through the furnace and after while through the depositing chamber), by the deposition, of tin oxide thin films on soda-lime glass substrates of large dimensions (400 mm x 400 mm x 2 mm).

Approach to the problem

Basically, I was confronted with studying of Chemical Vapor Deposition in general. Theory says that CVD process is feasible under the following conditions: soda lime glass (400x400x2 mm) has to be preheated up to approximately 400°C and after heating is prepared to be deposited under atmospheric pressure ($p=101325$ Pa) by gas mixture of SnCl₄ + 2H₂O in depositing chamber. It was from crucial significance to determine the time necessary for heating of the soda lime glass substrate. Using that time it was possible to calculate constant velocity for moving belt on which was substrate placed. Finally it has had to be synchronized time which glass spent under the infra red radiators - furnace and in depositing chamber due to constant velocity of moving belt.

The main idea of problem simplification was to split CVD into two parts: heating and deposition. In first part of problem determination was modeled time necessary for heating of the substrate and in second part occurred 3D Computation Fluid Dynamics (CFD) simulations. Due to small velocity of moving belt, there appeared some assumptions. There were ignored boundary conditions in heating process on the edges of the glass substrate:

1. dispersion of infra red beams – energy lost
2. non uniform heated surface – bad pattern for the intelligent window
3. length of substrate caught by deposition chamber after furnace is on constant temperature during deposition

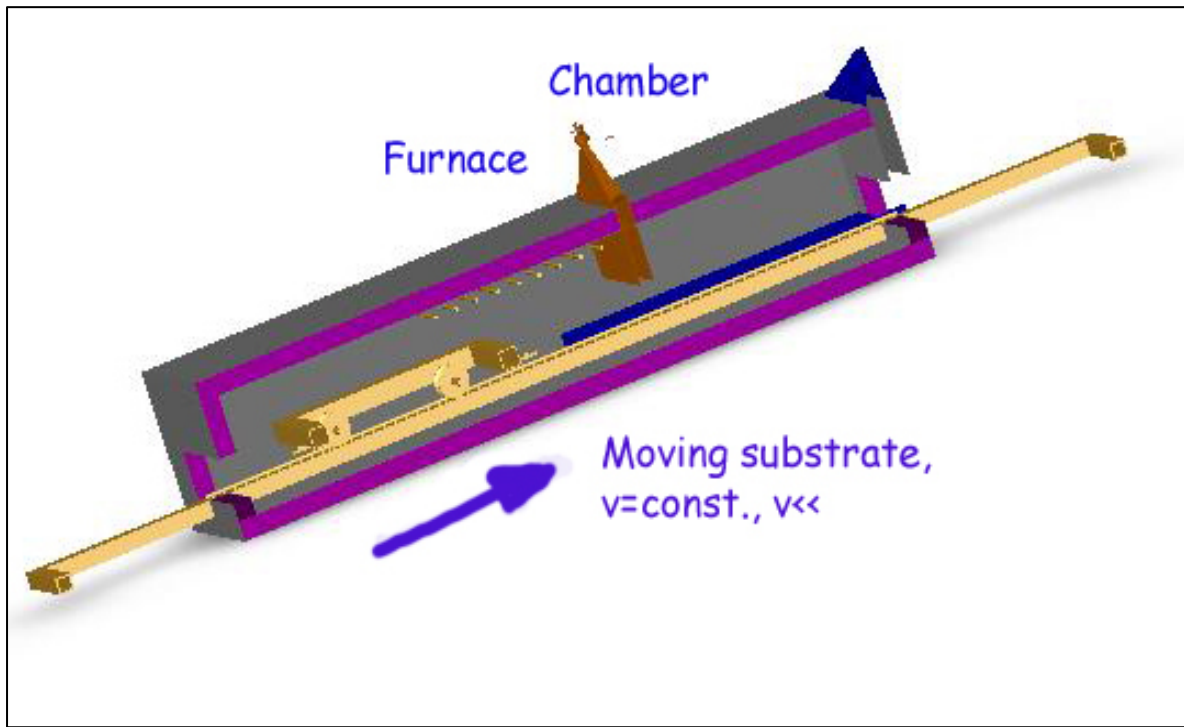
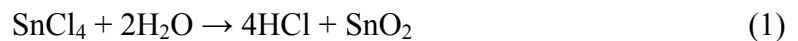


Figure 1.

The system consists of two parallelepiped-like chambers: the furnace containing the IR lamps in which the glass is heated (1) and the chamber where the deposition occurs

In the chamber (1) is used a mathematical model for determining the necessary time for heating the substrate with IR radiators, while in chamber (2) are made 3D simulations of the CVD process.

Basic chemical reaction which occurs on soda lime glass surface is given below:



Tin chloride SnCl_4 appears in gas phase and H_2O appears like water vapor. SnO_2 tin dioxide is finally wanted product of deposited semi-conductive layer and there is also unwanted product of hydrogen chloride which has to be safely removed from depositing chamber.

Mathematical model of heating system with IR-radiators

Adopted was "two parallel plates" model for radiation due to nearness of IR radiator surface and soda lime glass surface which is also explained in Figure 2. Infra red radiators IR were considered like a heating plane surface of a constant temperature 900°C .

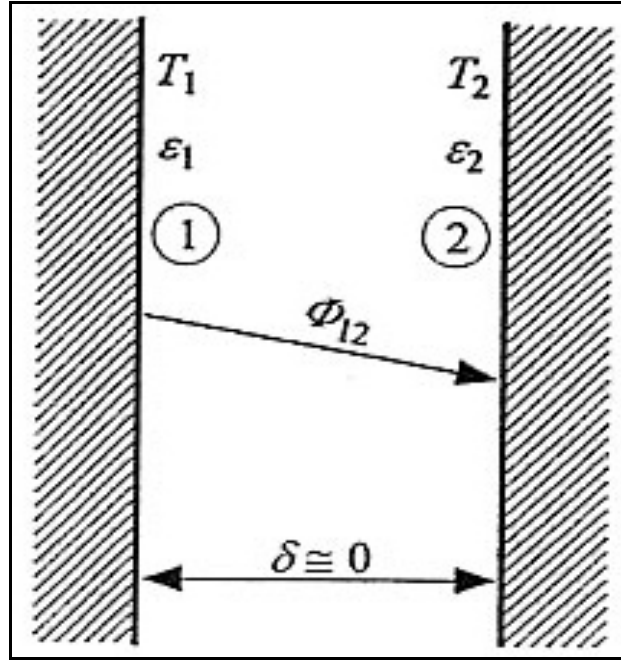


Figure 2.

Basic equation for the heat flow from the IR's to the substrate:

$$\Delta\Theta_{12} = mc \frac{\Delta T}{t} [W] \quad (2)$$

The heat flow is given by the equation for radiation between two flat surfaces:

$$\Delta\Theta_{12} = \frac{A\sigma(T_1^4 - T_2^4)}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1} [W] \quad (3)$$

By equalizing these equations and transferring into infinitesimal form:

$$\rho\delta c \frac{dT}{dt} = \frac{\sigma(T_1^4 - T^4)}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1} \quad (4)$$

Final form of the basic integral equation for this system is given by equation (6):

$$T = \frac{\sigma}{\rho\delta c \left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1 \right)} \int_{t=0}^{t=t_1} (T_1^4 - T^4) dt \quad (5)$$

Solving that equation from $t = 0$ up to 150 s time depended substrate temperature is shown below:

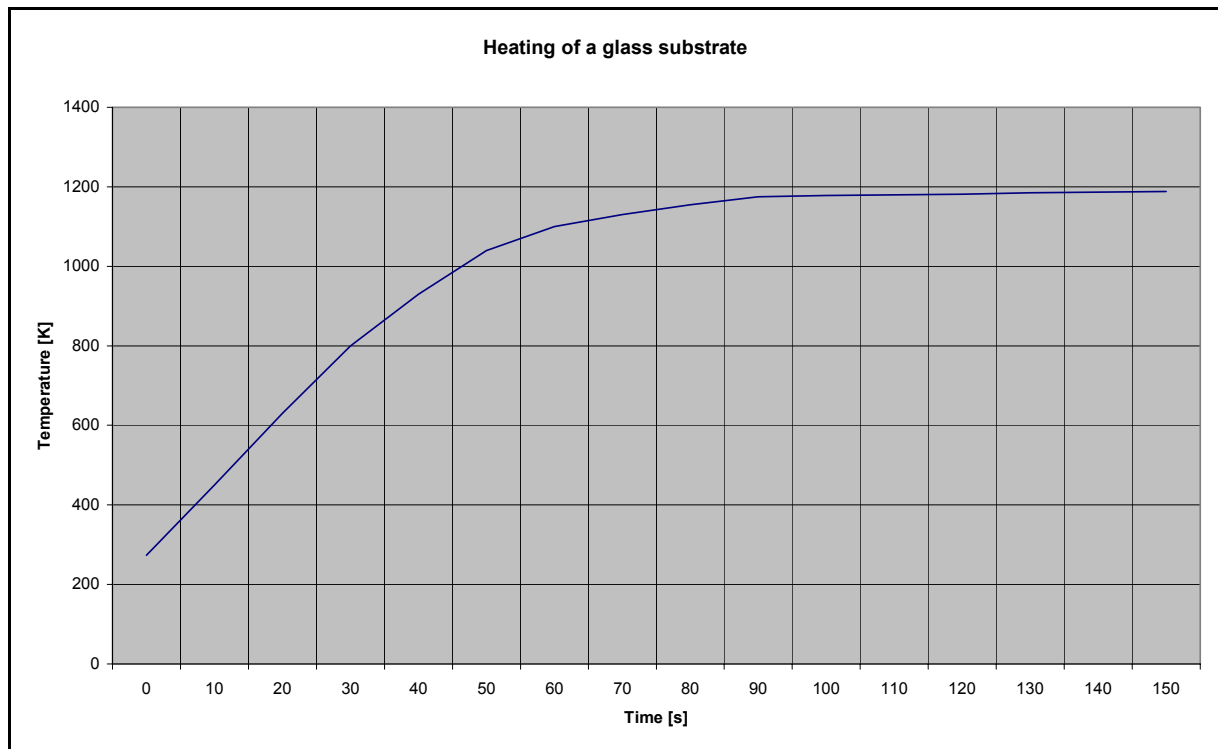


Figure 3.

According to our model it is necessary to heat the substrate for approximately 23 s to achieve 400°C (soda-lime glass 2 mm thick), which is supposed to be an optimal temperature for Chemical Vapor Deposition.

3D-CFD simulations of CVD process

Chemical Vapor Deposition (CVD) is complex process which at the same time includes accurate modeling of time - dependent hydrodynamics, heat and mass transfer and chemical reactions (including wall surface reactions).

Modeling the reactions taking place at gas-solid interfaces is complex and involves several elementary physico-chemical processes like adsorption of gas-phase species on the surface, chemical reactions occurring on the surface and desorption of gasses from the surface back to the gas phase.

Methodology

- Creating basic geometry in **Gambit**
- Splitting real, finite, volume into infinite derivable ''control volumes'', ''meshing''
- Defining boundary zones (inlet, outlet, surface and wall)
- Exporting designed model into solver **Fluent** where the final model definitions occurred

- Applying numerically algorithm for solving system of differential equations assuming a priori values for temperature, velocity, pressure, surface deposition ratio and correcting them in each iteration
- The system of equations is solved when the final difference, called "Residual", between obtained results and input boundary condition is smaller then initial value given by user.

Differential equation system

Continuity equation:

$$\frac{\partial \rho}{\partial t} = - \frac{\partial(\rho v_j)}{\partial x_j} \quad (6)$$

Momentum conservation equations:

$$\frac{\partial(\rho v_i)}{\partial t} = - \frac{\partial(\rho v_j v_i)}{\partial x_j} + \rho f_i - \frac{\partial p}{\partial x_i} + \frac{\partial \sum_{ji}}{\partial x_j} \quad (7)$$

Energy conservation equation:

$$\frac{\partial}{\partial t} \left[\rho \left(\frac{v^2}{2} + u \right) \right] = - \frac{\partial}{\partial x_j} \left[\rho v_j \left(\frac{v^2}{2} + u \right) \right] + \rho f_i v_i - \frac{\partial(\rho v_i)}{\partial x_i} + \frac{\partial(\sum_{ji} v_i)}{\partial x_j} + \frac{\partial}{\partial x_i} \left(\lambda \frac{\partial T}{\partial x_i} \right) \quad (8)$$

Equations (6)-(8) define only mass and heat transfer of the gasses along the chamber while equation (9) presents conservation species transport equation:

$$\frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i$$

where below is given explanation for each symbol in equation:

Y_i - the local mass fraction of each species

R_i - the net rate of production of species i by chemical reaction

S_i - the rate of creation by addition from the dispersed phase plus any user-defined sources

$\vec{J}_i$ - is the diffusion flux of species i

Problem definition for model No1.

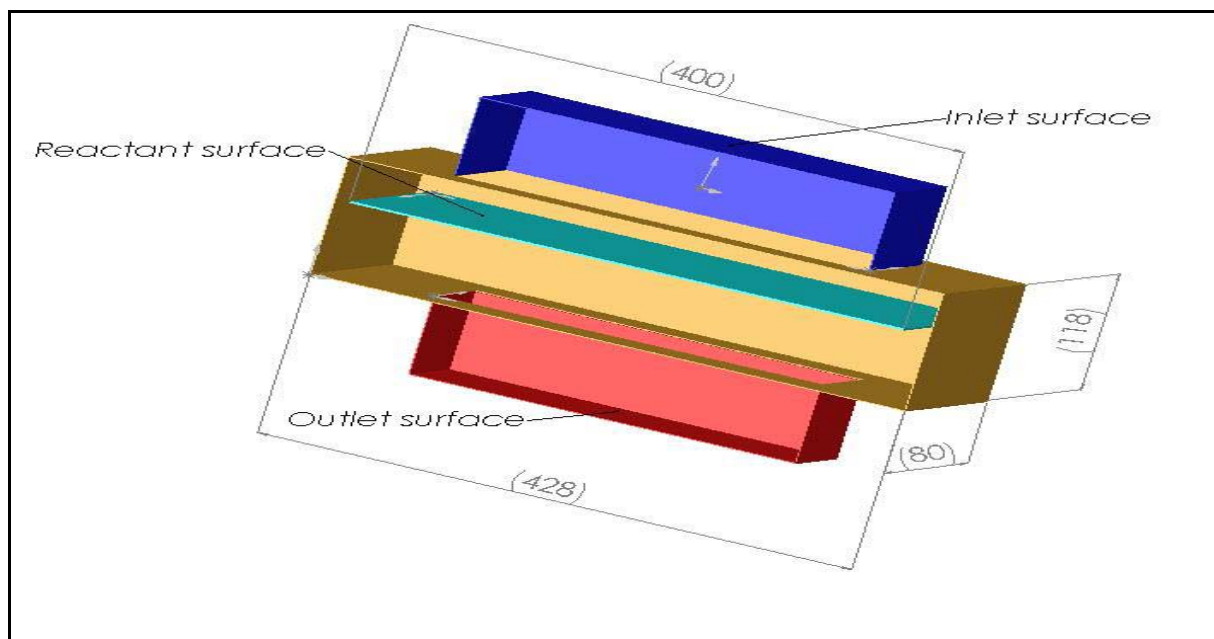


Figure 4.

As is shown in figure 4 the observed control volume of deposition chamber consists of following significant surfaces: inlet, reactant and outlet surfaces. The mixture of reactant gasses, $\text{SnCl}_4 + 2\text{H}_2\text{O}$, flows into deposit chamber, react on heated reactant surface and goes out through the outlet surface. Model assumption which was applied is that temperature of the reactant surface is constant along the width of the chamber and for first simulation that velocity of reactant surface is 0.

The big significance in this researching work was determination of the material properties of an exotic chemical species and reactions.

Material properties

Parameter	HCl	SnCl ₄	SnO ₂
Name	Hydrogen-Chloride	Stannic-Chloride	Stannic-Oxide
Density (kg/m ³)	1.5599	2234	6930
Cp (J/kgK)	0.00798	0.6345	0.3489
Thermal conductivity (W/mK)	0.0159	66.8	93.1295
Viscosity (kg/ms)	1.31e-05	0.00095	0.0075
Molecular weight (kg/kmol)	36.461	260.51	150.71
Standard state enthalpy (J/kg)	-5.7763e+08	-5.113e+08	-5.7763e+08
Standard state entropy (J/kgK)	186900	250600	49040
Reference temperature (K)	298.15	298.15	298.15
L-J characteristic length	3.711	3.711	3.711
L-J energy parameter	78.6	78.6	78.6
Degrees of freedom	0	0	0

Table 1.

References:

''Handbook of Chemistry and Physics, 77th Edition'', David R.Lide 1996-1997

Results of model No1

Thanks to excellent graphic user interface of Fluent, interpretation of obtained results was quite easy in colorized 3D perspective. From figure 5 we can see that red color present biggest surface deposition rate of SnO₂ expressed in (kg/m²-s). That was expected data due to biggest concentration of species mixture on reactant surface edge where the gases bypass the surface according to the outlet surface.

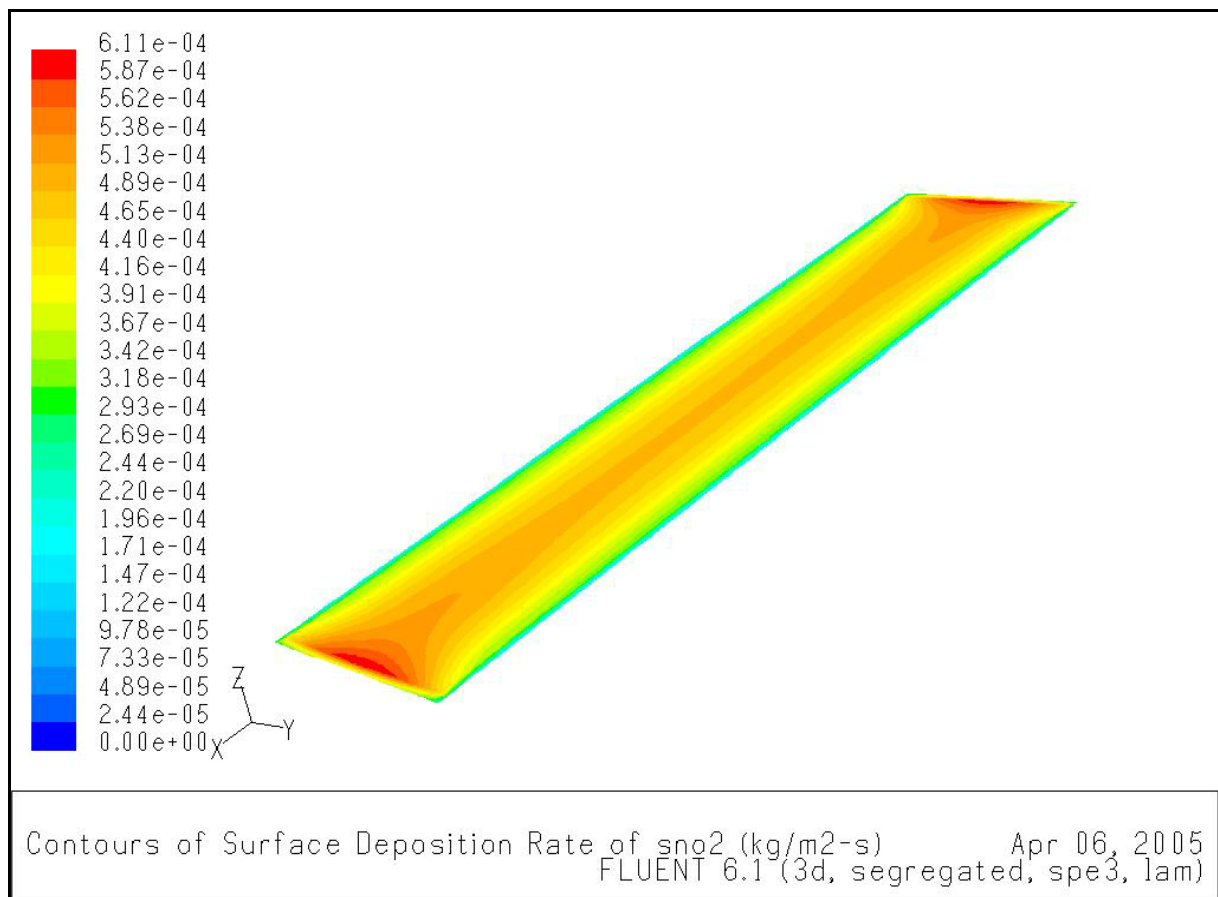


Figure 5.

In figure 6 is given 2D chart of surface deposition rate along the center line of reactant surface.

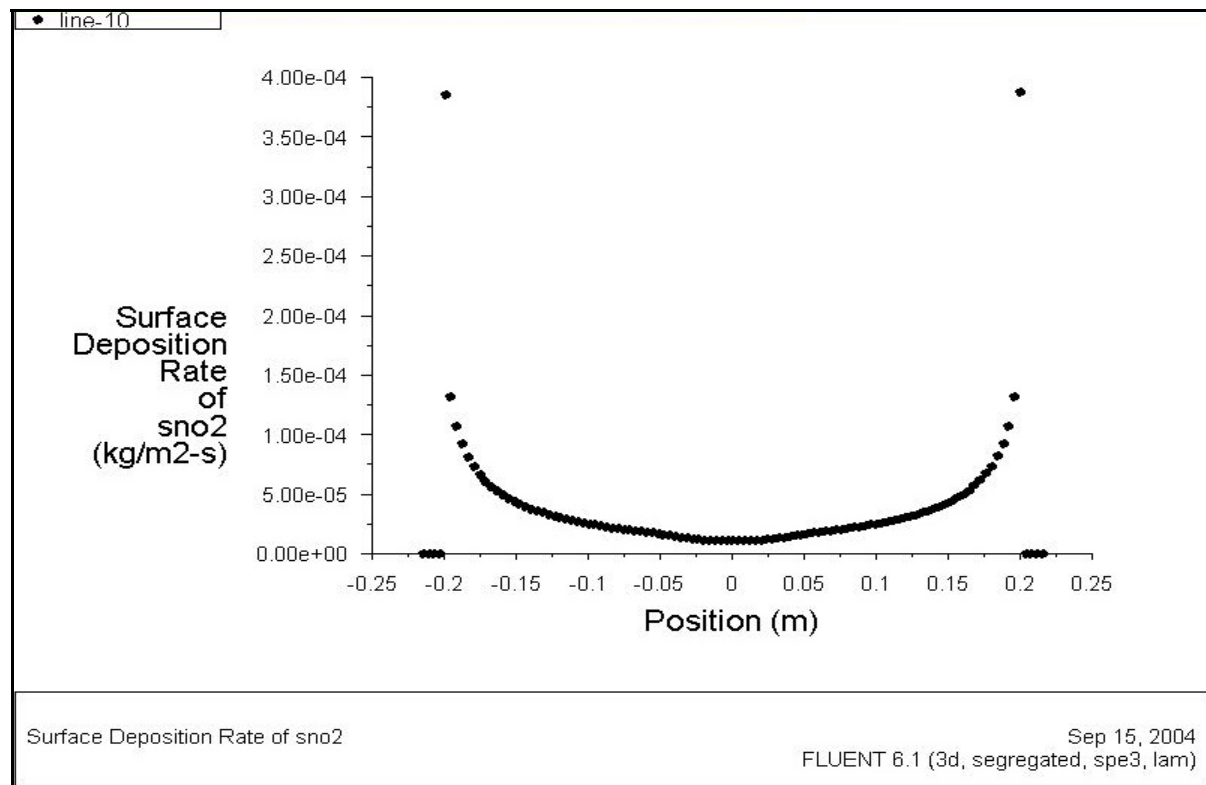


Figure 6.

As we can see, surface deposition rate of SnO_2 along the substrate surface is not uniform 'enough' (deposition curve should be flat, not parabolic shaped). Main significance of simulations is to obtain as much as it is possible uniform deposited layer along the soda - lime glass substrate. Therefore, depositing chamber model geometry and positioning of observed surfaces improvement should occur!

Problem definition for model No2

Basic idea to change chamber construction was to redirect gases flux above the substrate surface in transversal direction instead of old, vertical and width of substrate is in total caught by gases inlet so there is avoided possibility of local gases concentration in some boundary areas above the substrate.

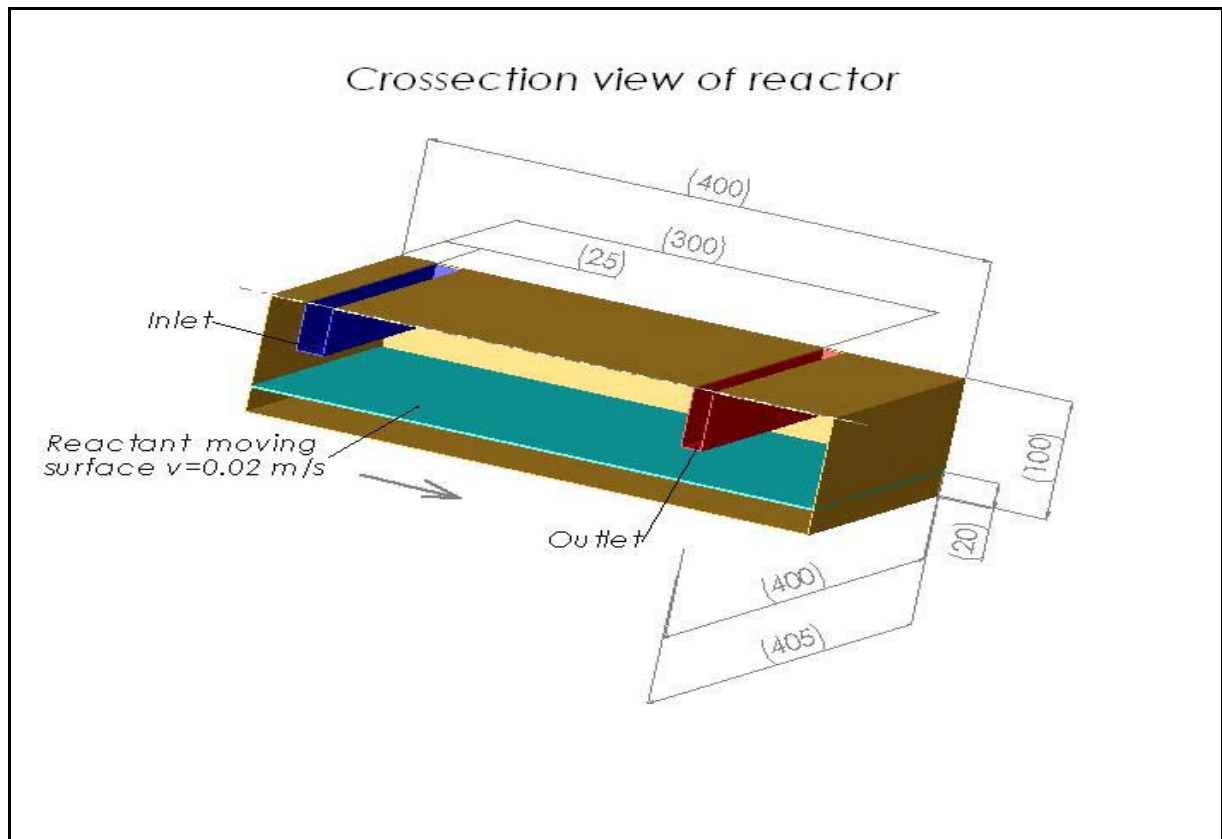


Figure 7.

Results of model No2

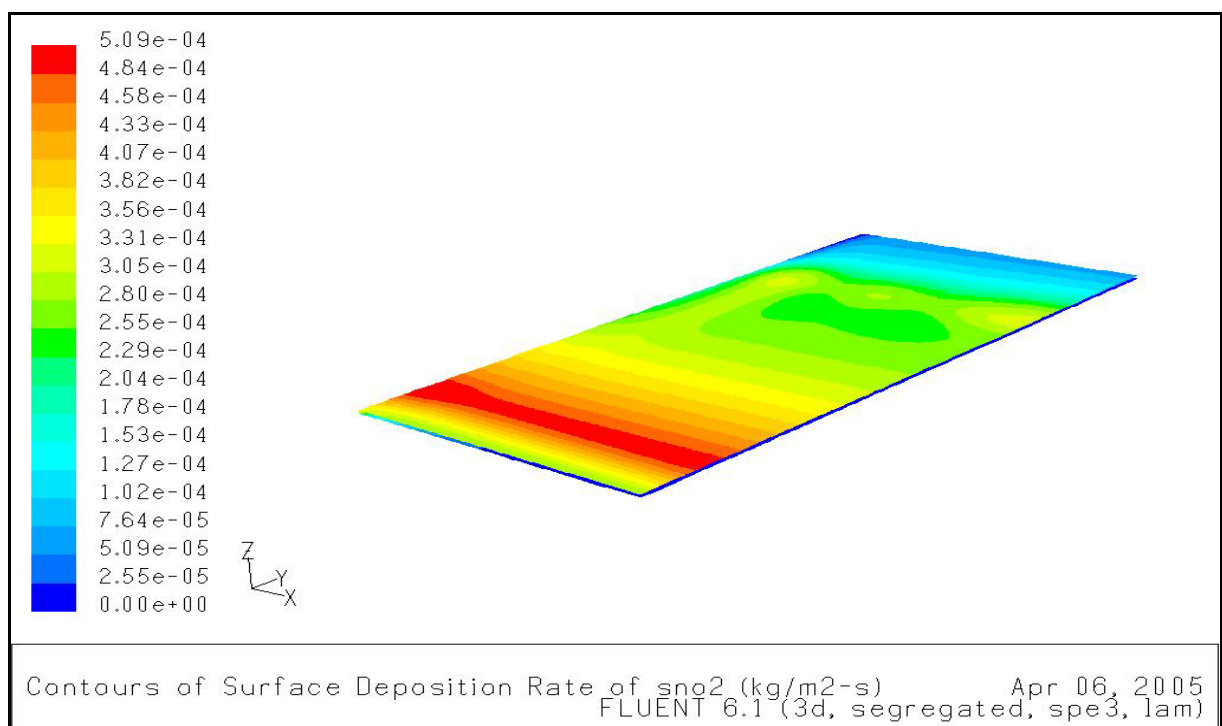


Figure 8.

From figure 8 we can see that geometry redesign was helpful in terms of deposition uniformity improvement. On coordination defined with vector (x {0.0025-0.403}, y=0.04, z=0.0222), where is the most red color, obtained was uniform deposition along the substrate width. Wanted aim of deposition uniformity was provided!

According to initial data from table 2, 2D chart of surface deposition rate is presented in figure 9.

Operating conditions		Boundary conditions INLET				Boundary conditions SURFACE		Boundary Con. OUTLET
p (Pa)	T (K)	v (m/s)	T (K)	Mass fractions		T (K)	v _y (m/s)	Outflow
				SnCl ₄	H ₂ O			
100000	303	0.08	573	0.4	0.3	673	-0.05	

Table 2.

2D Chart of SnO₂ layer along the line defined with (x {0.0025-0.403}, y=0.04, z=0.0222)

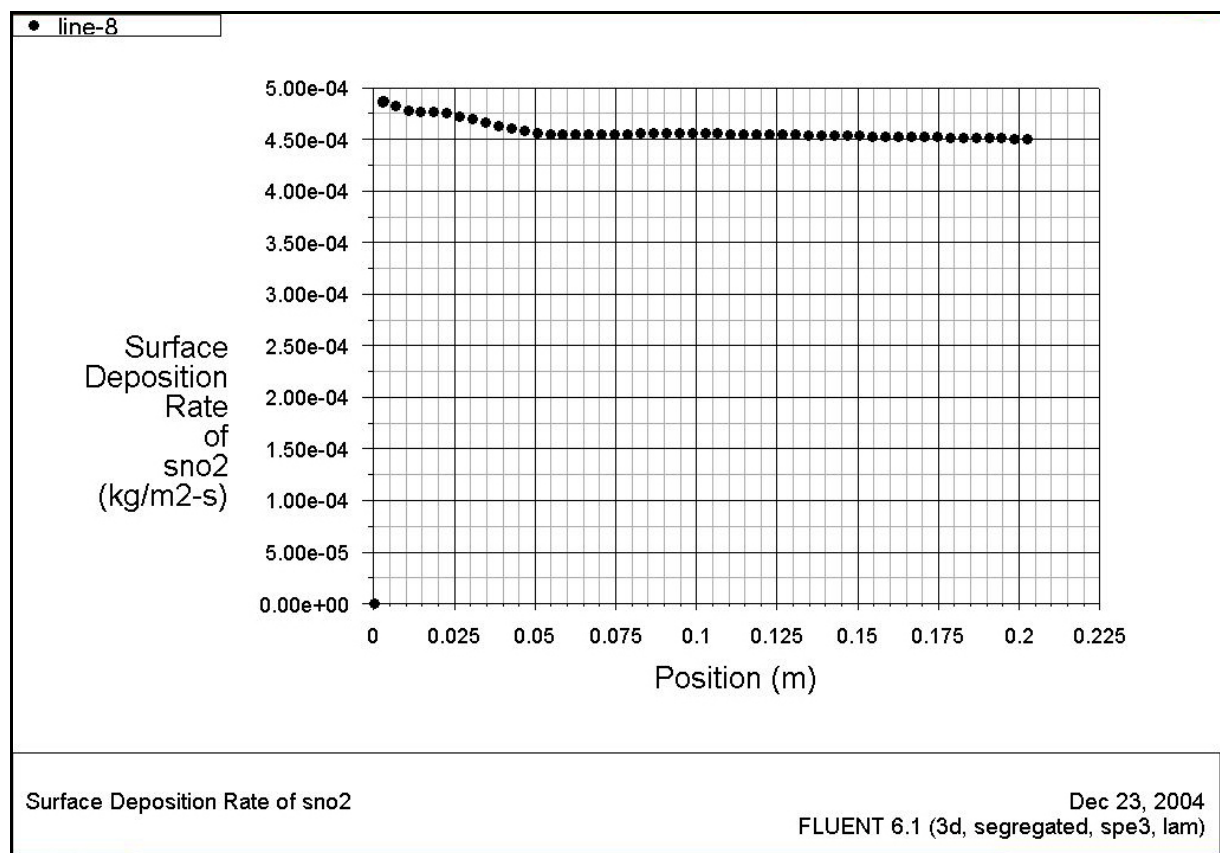


Figure 9.

Following examinations of model led to the inlet temerature modification as is shown in table 3.

Operating conditions		Boundary conditions INLET				Boundary conditions SURFACE		Boundary Con. OUTLET
p (Pa)	T (K)	v (m/s)	T (K)	Mass fractions		T (K)	v _y (m/s)	Outflow
				SnCl ₄	H ₂ O			
100000	303	0.08	473	0.4	0.3	673	-0.05	

Table 3.

2D Chart of SnO₂ layer along the line defined with (x{0.0025-0.403}, y=0.04, z=0.0222)

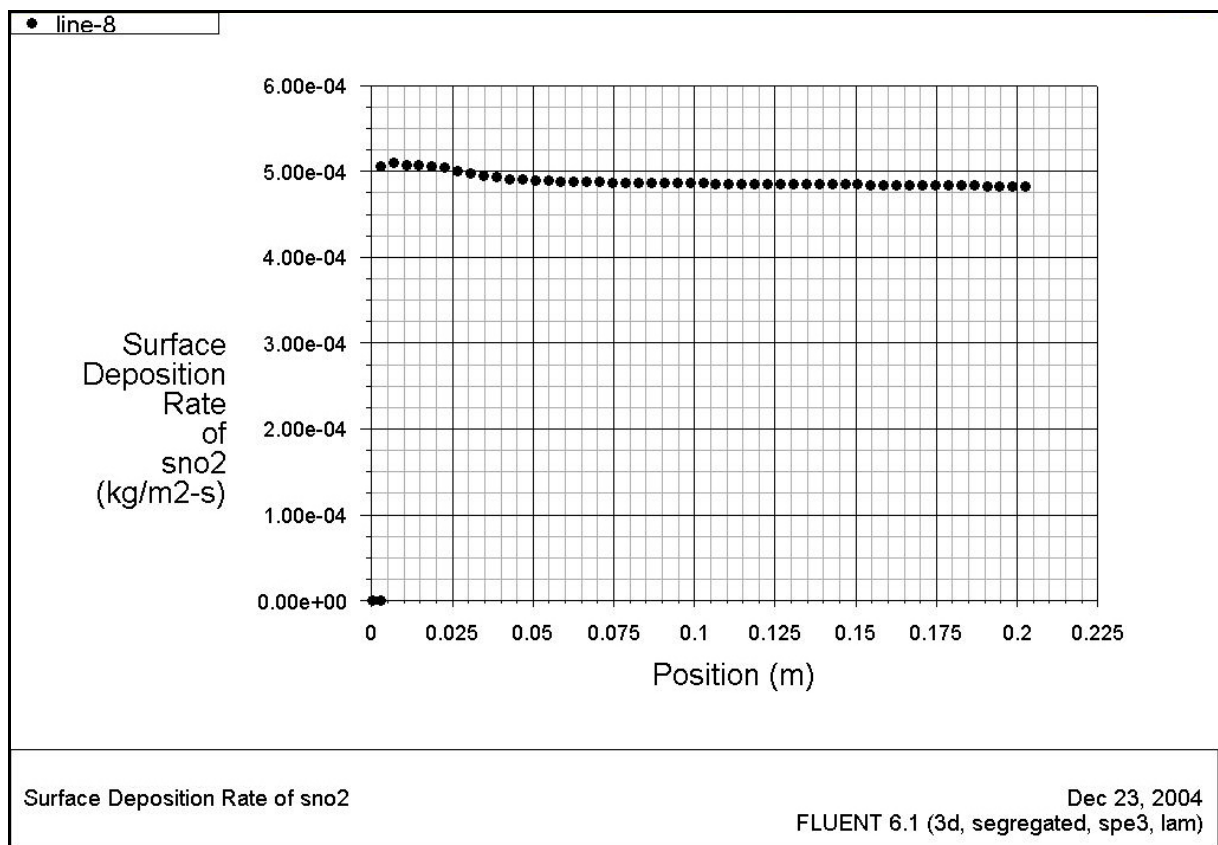


Figure 10.

We can perceive increase of surface deposition rate of SnO₂ (from 4.5e-04 (figure 9) to almost 5e-04 (figure 10)). Only by decreasing temperature of inlet gases (from 573 K to 473 K) we could notice improvement of deposition rate.

In following simulation by the temperature was also decreased and velocity of moving substrate. Deposition rate again increase what is shown in figure 11.

Operating conditions		Boundary conditions INLET				Boundary conditions SURFACE		Boundary Con. OUTLET
p (Pa)	T (K)	v (m/s)	T (K)	Mass fractions		T (K)	v _y (m/s)	Outflow
				SnCl ₄	H ₂ O			
100000	303	0.08	403	0.4	0.3	673	-0.02	

Table 4.

2D Chart of SnO₂ layer along the line defined with (x{0.0025-0.403}, y=0.04, z=0.0222)

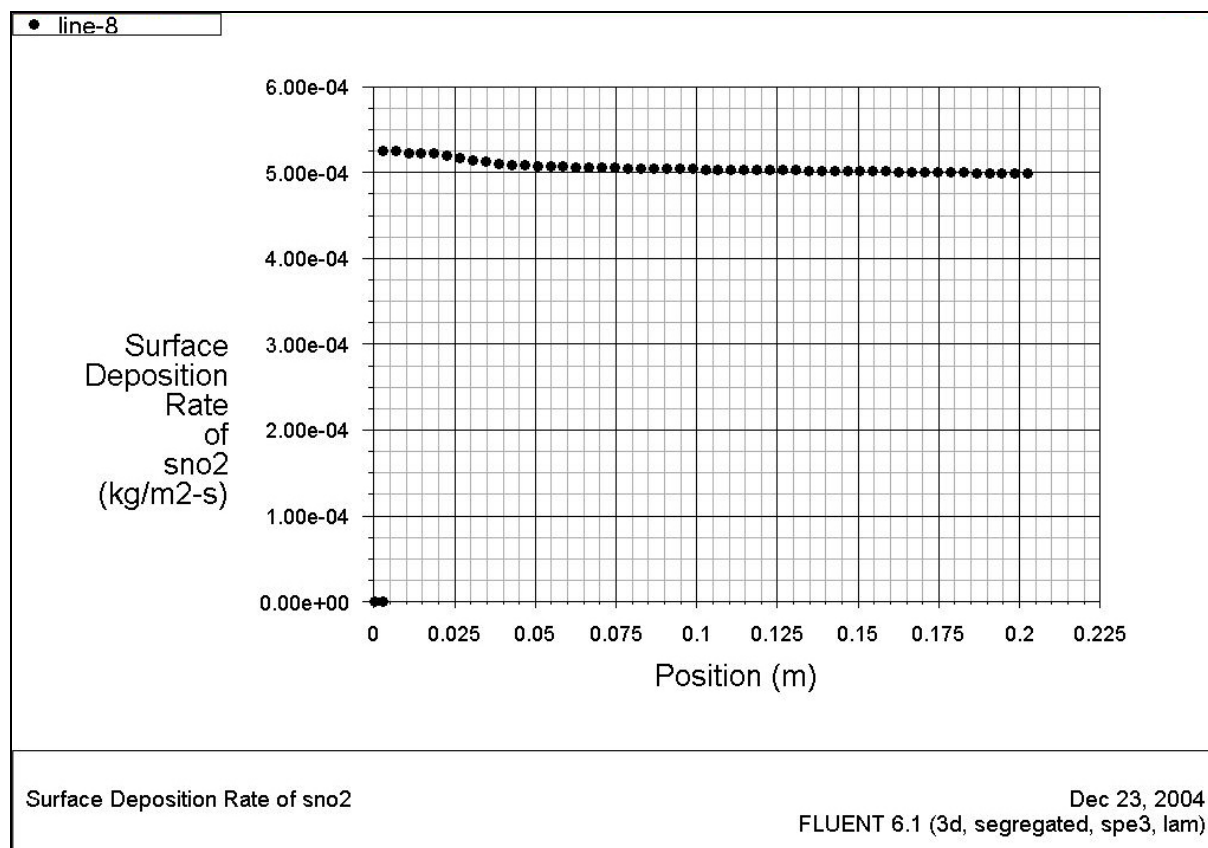


Figure 11.

For final simulation was again decreased velocity of moving substrate which just justified better deposition rate of SnO₂ along the soda lime –glass substrate.

Operating conditions		Boundary conditions INLET				Boundary conditions SURFACE		Boundary Con. OUTLET
p (Pa)	T (K)	v (m/s)	T (K)	Mass fractions		T (K)	v _y (m/s)	Outflow
				SnCl ₄	H ₂ O			
100000	303	0.08	403	0.4	0.3	673	-0.12	

Table 5.

2D Chart of SnO₂ layer along the line defined with (x{0.0025-0.403}, y=0.04, z=0.0222)

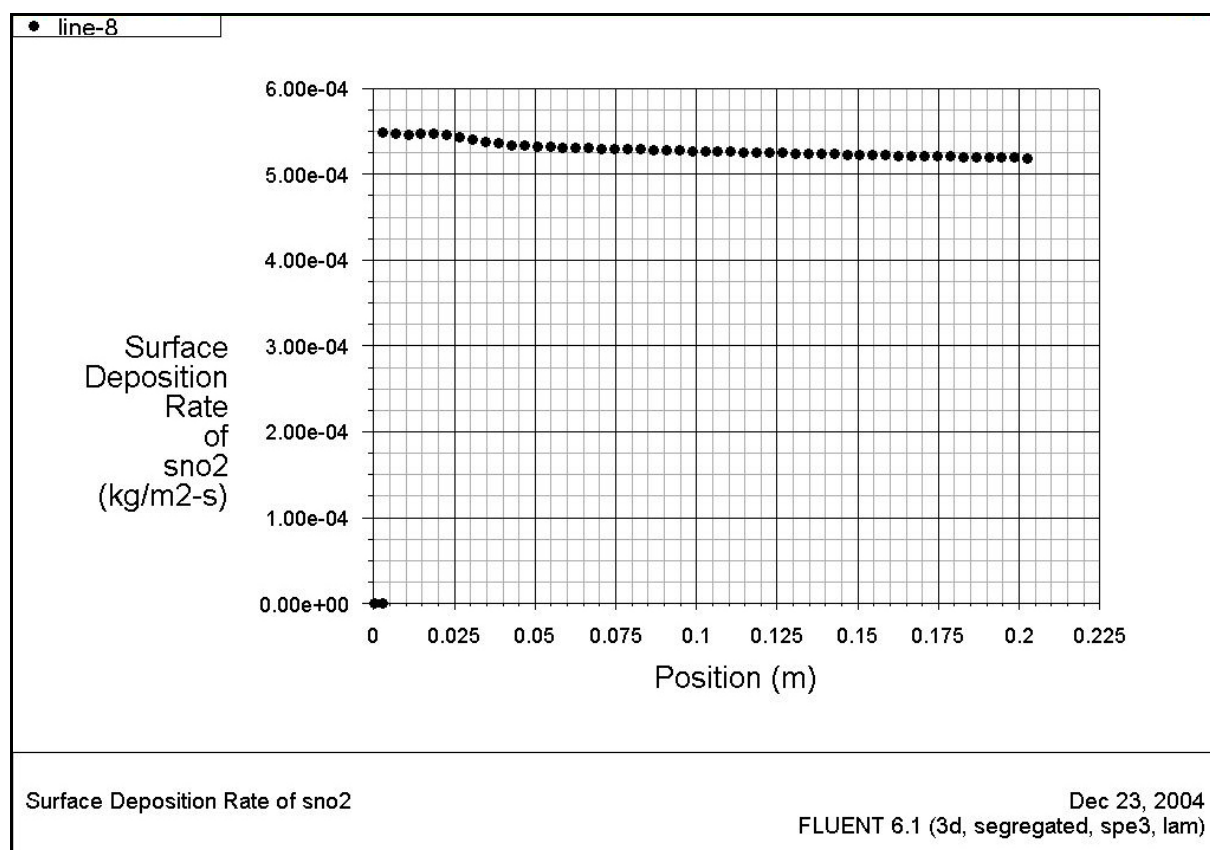


Figure 12.

Conclusion

Although it was used very simple chamber geometry, the simulation showed to be helpful if we intend to optimize the uniformity of the deposited layer, throughput and the yield of the coating glasses of large area. Further research will be focused on improving geometry of the chamber and optimizing parameters of the process to get better uniformity of the deposited layer along the substrate surface. Enhancement of the model could occur also by modeling of inlet nozzles which were out of time for this project.

References

1. Alaide P.Mammana, Thebano E.A.Santos and Marcos H. M. O. Hamanaka and Simone C. Trippe, "Thermal behavior of SnO₂ thin films obtained by vapor decomposition", 16th International Vacuum Congress (IVC-16), Venice, June 28th to July 2nd, 2004.
2. Admilson F. Botaro, Fátima C. Reis, Marcos A. Schreiner e Alaide P. Mammana, "Obtenção de SnO₂ por decomposição de vapores: estudo da cinética da reação", Anais do VI Seminário Iberoamericano de Mostradores de Informação, Fortaleza, 29 de setembro a 3 de outubro de 2003, pp. 28.
3. "FLUENT & GAMBIT", Users manual and on-line tutorial guide, © Fluent Inc. 2003-01-24.
4. "Handbook of Chemistry and Physics, 77th Edition", David R. Lide, 1996 – 1997.
5. "Thermodynamics I & II", Antun Galovic, Ed. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Croatia.
6. "Regulation of the Process", V. Serman, Ed. Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Croatia.