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Invited Paper

NUMERICAL SIMULATION APPLIED TO CHEMICAL VAPOUR DEPOSITION PROCESS. RAPID THERMAL CVD AND SPRAY CVD

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The paper gives an overview of the different applications of the numerical simulation in chemical vapour deposition (CVD) process and equipment. In particular, emphasis will be given to the modelling of Rapid Thermal Low Pressure CVD and to the perspective of modelling Spray CVD.

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1. Introduction

Chemical vapour deposition (CVD) is a widely used method for depositing thin films of a large variety of advanced materials. Applications of CVD range from the fabrication of microelectronic devices to the deposition of protective coatings but also optoelectronic films, decorative coatings and so on [1]…

In a typical CVD process, reactant gases (often diluted in a carrier gas) at room temperature enter the reaction chamber. The substrate can be heated in resistive oven, by hot plate or by IR lamps. So, the gas mixture is heated as it approaches the deposition surface.

Depending on the process and operating conditions, the reactant gases may undergo homogeneous chemical reactions in the vapour phase before striking the surface. Near the surface, thermal, momentum, and chemical concentration boundary layers form as the gas stream heats, slows down due to viscous drag, and the chemical composition changes. Heterogeneous reactions of the source gases or reactive intermediate species (formed from homogeneous pyrolysis) occur at the deposition surface forming the deposited material. Gaseous reaction by-products are then transported out of the reaction chamber.

Actually, there are various CVD methods [2]: Atmospheric pressure CVD, the first to be experimented, Low Pressure CVD when reactive gases are allowed to be evacuated through vacuum pump, then Plasma Enhanced CVD where the energy needed to achieve the chemical reaction comes from both thermal and plasma sources; (as a consequence, this method leads to lower deposition temperature); Rapid Thermal CVD (RTCVD) where the energy originates from IR lamps. The main advantage of the RTCVD method is to reduce the thermal budget thanks to very short response time of IR radiative heating. In Spray CVD, the precursor is in liquid phase and is sprayed onto the substrate. The advantage of this method is not in term of thermal budget (because deposition temperatures are usually low) but in term of covered surface because this method can be carried out on very large surfaces and, also, continuously.

2. Numerical simulation

New CVD processes are increasingly complex, with stringent requirements that make it more difficult to commercialize them in a timely fashion. In the past, design optimization of technical systems was usually based on the experience of the designer, who analysed the system

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performances and modified individual system parameters. This kind of optimization becomes more and more difficult with an increasing number of design parameters. The advent of powerful computing capability at relatively low cost has spurred the development of numerical models. Modelling can significantly speed up the design and optimization stages. That is why the use of numerical methods for parameter optimization combined with simulation is a promising approach to overcome this problem.

Governing equations required for the simulations are the conservation of mass (continuity equation), momentum (Navier–Stokes equation) and energy [3]. Most of the equations can be expressed in the form of a generalized transport equation (conservation equation) with the transient term, the convective term, the diffusion term and the source term, respectively:

$$\frac{\partial \rho \phi}{\partial t} + \nabla \cdot \left(\rho \vec{V} \phi \right) = \nabla \cdot \left(\Gamma \nabla \phi \right) + S_{\phi} \tag{1}$$

where ρ is the density, t is the time, V is the volume, ϕ is the general flow variable, Γ is the diffusion coefficient and S_{ϕ} is the source term for the general flow variable. More details concerning the mathematical background can be found in educational literature [3-4].

A numerical method to solve these Partial Differential Equations (PDE's) consists of their discretization on a computational grid, the formation of a set of algebraic equations, and the solution of the algebraic equations. The finite-volume approach is generally adopted due to its capability of conserving solution quantities [5]. The solution domain is divided into a number of cells known as control volumes. The governing equations are numerically integrated over each of these computational cells or control volumes.

Numerous numerical models have been developed to simulate the CVD process and a variety of specialized Computational Fluid Dynamic (CFD) tools is available: FLUENT [6], PHOENICS [7], Star-CD [8], CFD'ACE [9]. FLUENT'S CFD software is commercialised since 1980. It provides the important physics required for CVD reactor modelling, including gas phase/surface reaction chemistry, multicomponent and Soret diffusion, natural convection, non-grey radiation with participating media, and the ability to include fully compressible flow regions. PHOENICS is commercialised by CHAMS since October 1981. PHOENICS is supplied with five models of radiation, namely: a. the composite-flux model, which is also known as the six-flux model, b. the composite-radiosity model, which is similar to the P-1 spherical-harmonic model, c. the Rosseland diffusion model, which, in PHOENICS, is derived from the radiosity model, d. the IMMERSOL model, which is a more complete version of (b), e. the Surface-To-Surface radiation model. Chemical reactions are simulated by PHOENICS in several ways, including: CHEMKIN a public-domain code established by Sandia National Laboratories [10]. However, such a tool must be able to capture in detail both the chemical kinetics and the complex fluid flows taking place. To meet the challenge of merging complex chemistry with complex fluid flows, the CD-ADAPCO Group has incorporated several new chemistry features in its industry-leading STAR-CD software. The resulting joint product, STAR-CD/KINetics, combines the CFD and geometry-handling strengths of STAR-CD with components of CHEMKIN's leading-edge technology for treating complex coupled chemical kinetics and molecular transport.

CFD'ACE from ESI Group provides advanced simulation tools which employ state-of-the-art numerical schemes and the most advanced physical models to provide powerful multiphysics solutions to a wide variety of complex industrial applications. It includes advanced pre-processing program (GEOM) and post-processing program (VIEW). GEOM supports all grid technologies including multi-block structured, general polyhedral unstructured, arbitrary interfaces, and moving and deforming grids. A unique feature of CFD-GEOM is the support for the scripting language Python [11]. All geometry and mesh functionality is accessible from Python script language, enabling the end-user to create custom parametric script templates for his analysis case. The geometry/mesh templates can be used for automated parametric or optimization runs. CFD-VIEW is interactive graphics program for post-processing numerical results from CFD'ACE. It provides an easy-to-use and interactive environment with many graphics tools to visualize the flow physics, animate transient data sets, as well as extract data relevant to engineering design. It also uses the Python scripting language for customization and automation of the tool by the end-user.

The flow solver (ACE) is made up of several modules including: Fluid Dynamics, Heat Transfer, Radiation, Turbulence, Chemistry, Electrochemistry, Biochemistry, Free surface (Volume Of Fluid), Spray, Cavitation, Two Phases, Electromagnetics, Plasma, Boltzmann Kinetics, Structural Dynamics and user defined. Each one of these modules is tightly integrated into the CFD'ACE framework for efficient execution, including parallel processing, dynamic memory, and data management. This software is especially convenient for designing and optimizing semiconductor equipment and processes such as CVD. The commercially available multi-physics software package CFD-ACE provides the unique capacity to perform high fidelity three-dimensional simulations of heat and mass transport with complex multi-step gas-phase and surface reactions for industrial applications.

3. Raport thermal CVD

A previous study shows that CFD'ACE leads to the best results for modelling CVD so the following of this paper will be illustrated by application of this software [12].

In order to optimize the CVD process, the first concern is to take into account the reactor geometry then to resolve the Partial Differential Equations (PDE's) governing each phenomenon.

RTCVD systems are single-substrate (wafer), cold-wall chambers that utilize radiant heat sources to rapidly heat up the substrate at high temperature for short times. A commercial RTLPCVD system is shown in Fig. 1 [13] and the corresponding grid is shown in Fig. 2.

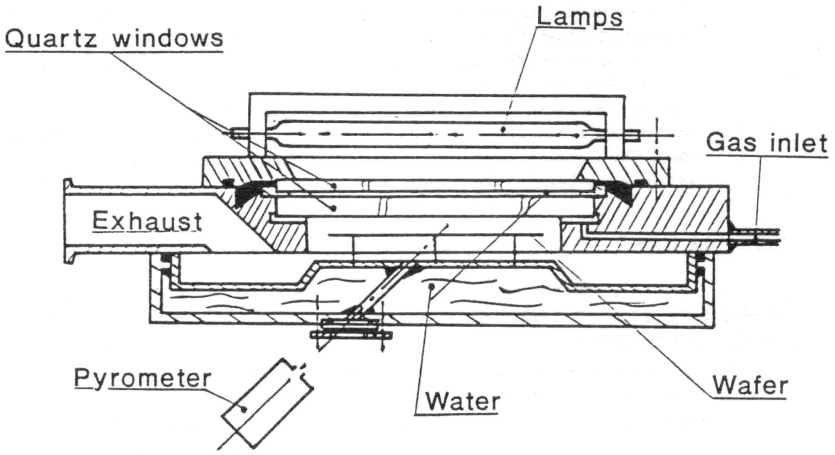


Fig. 1. Scheme of the RTLPCVD reactor FAV4 - JIPELEC.

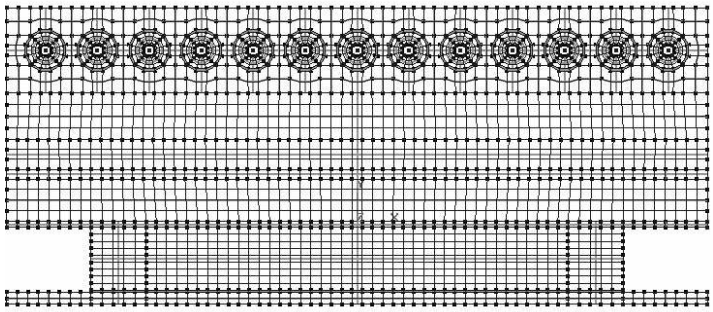


Fig. 2. Geometry of the RTLPCVD reactor FAV4.

One of the main technological hurdles that Rapid Thermal Process (RTP) must overcome is that of heating the wafer uniformly. So the phenomena to be modelled are flow and heat transfers.

Activating the Flow Module implies the solution of the velocity field by solving for the x, y, and z momentum equations, and the pressure field by solving the pressure correction equation.

Activating the Heat Transfer Module implies the solution of the total enthalpy form of the energy equation. Many types of heat transfer analysis can be performed with the Heat Transfer module, from basic conduction/convection to complex radiation modelling [14]. In the case of RTCVD, the substrate heating is performed through infrared lamps so the integro-differential radiative heat transfer equation for an emitting-absorbing and scattering grey medium has to be solved:

$$(\Omega \cdot \nabla) I(r, \Omega) = -(k + \sigma) I(r, \Omega) + k I_b(r) + \frac{\sigma}{4\pi} \int_{\Omega' = 4\pi} I(r, \Omega) \Phi(\Omega' \rightarrow \Omega) d\Omega' \tag{2}$$

where Ω is the direction of propagation of the radiation beam, I is the radiation intensity which is a function of both position *(r)* and direction (Ω), κ and σ are the absorption and scattering coefficients respectively, I_b is the intensity of black body radiation at the temperature of the medium and Φ is the phase function of the energy transfer from the incoming direction (Ω') to the outgoing direction (Ω). The term on the left hand side represents the gradient of the intensity in the specified direction (Ω). The three terms on the right hand side represent the changes in intensity due to absorption and out-scattering, emission and in-scattering respectively.

The boundary condition for solving the above equation may be written as:

$$I(r, \Omega) = \varepsilon I_b(r) + \frac{\rho}{\pi} \int_{n \cdot \Omega < o} \left| n \cdot \Omega' \right| I(r, \Omega') d\Omega' \tag{3}$$

where I is the intensity of radiant energy leaving a surface at a boundary location, ε is the surface emissivity, ρ is the surface reflectivity, and n is the unit normal vector at the boundary location.

If the optical thickness of the participating medium is very thin, the right hand side of equation (2) is zero. The equation becomes:

$$E_s(r) - \frac{1}{\varepsilon} q_s(r) = \int_r K(r, r') g(r') \cos(r' - r, n) \cos(r - r', n') dr', \; (r \in \Gamma) \tag{4}$$

where E_s is the blackbody emission power, q_s, the surface radiation flux, g is the radiancy.

This is the base of the "surface-to-surface" method. Surface-to-surface method is a very efficient method suitable for applications that do not involve participating gases and require fast estimation of the radiative heat fluxes, such as in the underhood of an automobile. This model is only grey.

The Surface-To-Surface model does not account for any participating medium, hence radiation through semi-transparent solids cannot be handled.

The Discrete Ordinate Method (DOM)] is well suited for accurately predicting radiative heat transfer for most engineering applications [15]. It is particularly suited to applications such as combustion where the gases are participating. The model can be used for both grey and non-grey properties. In the Discrete Ordinate Method, equations (2) and (3) are replaced by a discrete set of equations for a finite (specified) number of ordinate directions. The integral terms on the right hand side of equation (2) is approximated by a summation over each ordinate. The discrete-ordinate equations may then be written as:

$$\alpha_m \frac{\partial I_{m\lambda}}{\partial x} + \beta_m \frac{\partial I_{m\lambda}}{\partial y} + \chi_m \frac{\partial I_{m\lambda}}{\partial_z} = -(k_\lambda + \sigma) I_{m\lambda} + k_\lambda \Delta F I_b + \frac{\sigma_\lambda}{4\pi} \sum_{m'} W_{m'} \phi_{m'm} I_{m'\lambda} \qquad (4)$$
$$m = 1,...M$$

where: ΔF is the fractional energy emitted in a wavelength band.

For the grey model, the subscript λ should be dropped from the above equation and ΔF becomes unity. In the non-grey model, the radiative properties are assumed to be functions of wavelength only. The Discrete Ordinate Method has problems with specular radiation. The ordinate set implemented in the Radiation module is symmetric only about the x, y and z coordinate axes. Hence the specular reflection boundary condition (used for symmetry) is accurately imposed only for boundaries that are aligned with the coordinate axes. It is not very accurate for optically thin media. The spectral distribution is subdivided into a finite number of bands within which the properties are assumed uniform. In reality these properties are not uniform and this can lead to inaccuracies. The radiative properties are also highly dependent on the wavelength of the light. Since uniform properties are assumed in a spectral band this can also lead to inaccuracies in the solution.

The radiative transfer equation can also be solved in the frame of a Monte Carlo approach by tracing photon bundles (or rays) through discrete control volumes, and by accounting for the various events (absorption, emission and scattering) occurring within each control volume. Rays are emitted from a surface and traced until they are absorbed by the same surface or any other surface.

The Monte Carlo Method (MCM) is considered one of the most accurate methods for the calculation of radiative heat transfer. This is because of its ability to treat all directions of radiative transfer in a continuous fashion (rather than along discrete directions, as in the Discrete Ordinates Method), and its ability to account for strong oscillations in the spectral radiative properties. In addition, it is the only method that can treat non-diffuse reflection from walls. Although the Monte Carlo Method can be used to predict radiative transfer in any scenario, this particular model was developed with the semiconductor material processing industry in mind. Thus, its strength is best realized for Rapid Thermal Processing and Rapid Thermal Chemical Vapour Deposition applications, and in general, for simulation of radiative heat transfer in semiconductor processing applications.

As an example, numerical simulations of the RTCVD apparatus shown in Figs. 1 and 2 are carried out through CFD'ACE by using the Flow, Heat and Radiation modules with Discrete Ordinate Method or Monte-Carlo Method. The temperature distribution can be seen on Fig. 3.

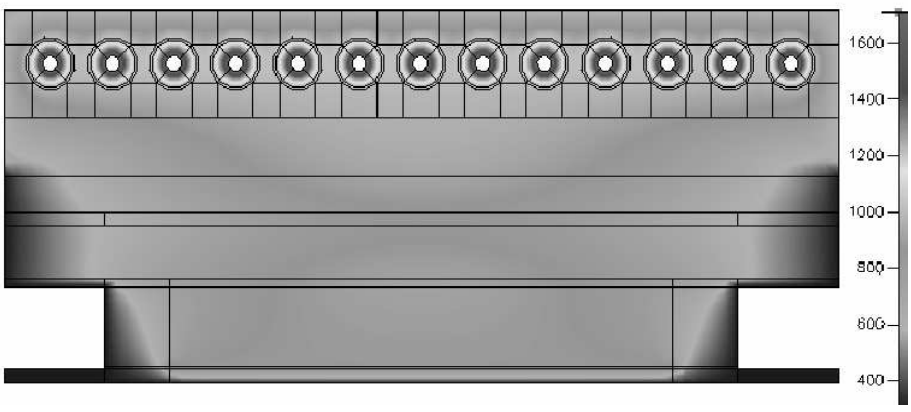
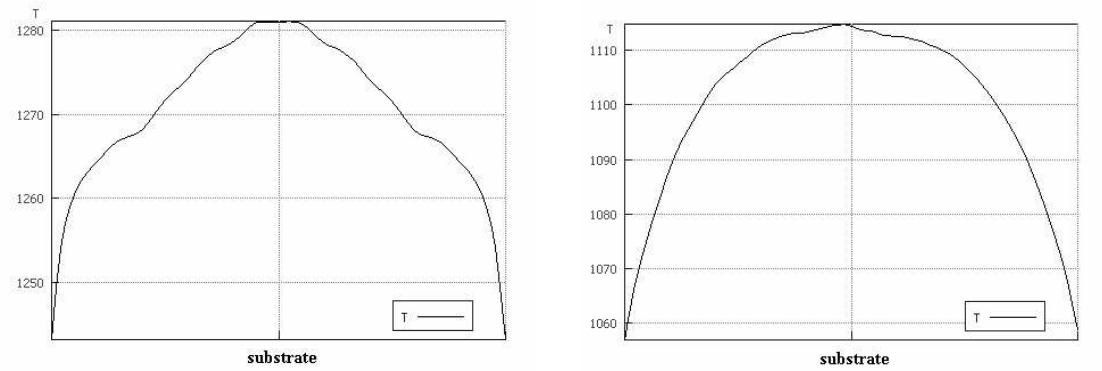


Fig. 3. Temperature distribution in the FAV4 reactor by using the Monte-Carlo radiation module of CFD'ACE (temperature is in Kelvins).

The temperature profile of the wafer surface can be obtained. A comparison between the simulation results by the two methods DOM and MCM is presented on Fig. 4.



(DOM) (MCM)

Fig. 4. Temperature profile along the substrate diameter, determined by both methods: DOM (on the left) and MCM (on the right).

A previous study has shown that the Monte Carlo method leads to temperature profile of the substrate in better agreement with the experimental ones either for the shape of the profile and the temperature difference between the centre and the edge of the substrate as can be seen in Fig. 5. To get the plots from Fig. 5, experimental measurements are performed by using five K-type thermocouples embedded in the backside of the silicon substrate, linearly arranged from the centre to the edge of the silicon substrate [16].

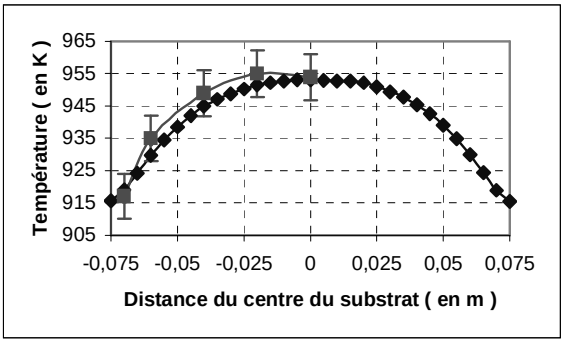


Fig. 5. Temperature profile along the substrate diameter: simulated by using Monte-Carlo method (grey squares) and experimentally measured (black squares).

Chemical reactions can also be taken into account. Activating the Chemistry module implies the solution of the mixture or species mass fractions, (the latter requiring solution of additional mass transport equations). The Chemistry module allows studying systems where both surface and gas-phase reactions occur. Reactions involving charged species (encountered in plasma reactors) can also be studied. It has two solution approach options: Mixture Mass Fractions and Species Mass Fractions. The Mixture Mass Fraction approach requires a solution of fewer transport equations than the Species Mass Fraction option. However, some models and fluid property options are not available for the Mixture Mass Fraction approach. The Mixture Mass Fraction approach is usually used for pure mixing problems and combustion reaction problems involving reactions, which are either in equilibrium, very fast (instantaneous), or can be modelled with a single global finite-rate reaction step. The Species Mass Fraction approach is the most general approach and encompasses all problems that can be solved using the Mixture Fraction approach except for models that include turbulence/chemistry interaction. The Species Mass Fraction approach requires the solution of a

transport equation for every species in the system. This approach is required for multi-component diffusion problems as well as problems, which contain surface reactions. The Species Mass Fraction approach must also be used if a multi-step finite rate gas-phase reaction is desired. The surface reaction models allow the calculation of deposition, etching, or catalytic reactions at surfaces. The reaction rates of individual steps can be computed either by using the sticking coefficient model, or by using a general finite-rate expression. In CFD-ACE, steps involving these two approaches can be mixed. Reaction mechanisms involving surface-adsorbed species and site coverage can be modelled using this feature.

As can be seen in Fig. 6, the simulated deposition rate can be obtained along the substrate diameter. This example is calculated for silicon deposition from silane in the RTCVD apparatus shown in Fig. 1.

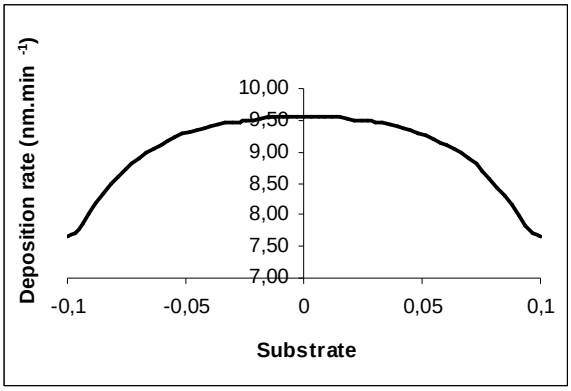


Fig. 6. Simulated deposition rate versus the substrate diameter.

4. Spray CVD

In the last years, ultrasonic spray CVD has emerged as an important alternative for conventional processes for depositing Transparent Conductive Oxide (TCO) [17]. On Fig. 7, typical Spray CVD equipment for the pyrosol process is presented [18]. The ultrasonic vibrator micronizes the liquid precursor, which forms a dense stream. The atomized solution is then transported using a carrier gas onto heated substrate. In this case, the key point is the homogeneity of the spray in order to deposit TCO on a large area.

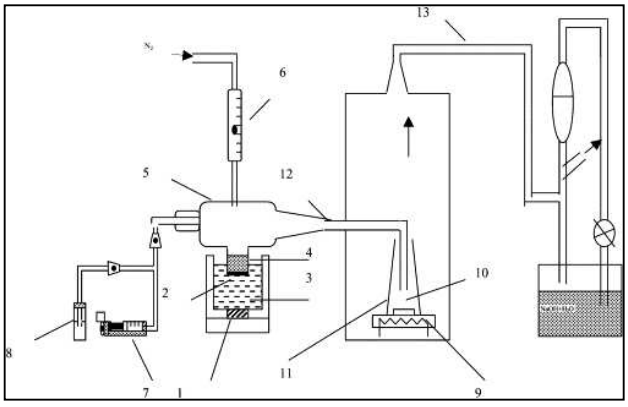


Fig. 7. Home-built Spray CVD apparatus - 1: Ultrasonic vibrator for spaying the precursor in 4, which is carried away towards the heated substrate in 10.

By using the Spray module of CFD'ACE, the discrete phase (droplets, particles, bubbles) tracking is achieved by solving the governing mass, momentum, and energy conservation equations in a Lagrangian frame of reference. The discrete phase is allowed to exchange mass (evaporation), momentum (drag), and energy (heat) with the continuous phase (surrounding ambient fluid).

The equation of motion for the droplet can be written as:

$$m_d \frac{d\upsilon}{dt} = C_D \rho (U - \upsilon)|U - \upsilon| \frac{A_d}{2} + m_d g + Sm \tag{5}$$

where m_d is the mass of the droplet and $\upsilon = u_i + u_j + w_k$ its velocity vector; u, u and w are the Cartesian velocity components; C_D is the drag coefficient; ρ and U are the density and the velocity of the surrounding gas, respectively; A_d is the droplet frontal area. The gravity vector is represented by g. Equation (5) accounts for the acceleration/deceleration of the droplet due to combined effects of drag with gas and body forces such as gravity. Additional mass sources, Sm, can be added to this equation.

As the droplet moves through the surrounding medium, it absorbs latent heat and evaporates. The rate of evaporation is modelled as:

$$\dot{m}_{e\upsilon} = 2\pi d \rho \Gamma_m Sh \ln(1 + B_m) \tag{6}$$

where Sh is the Sherwood number, Γ_m is the mass diffusion coefficient for the gas, and B_m is known as the Spalding number.

In this module, the volume displaced by the droplets is neglected so the model is applicable for dilute sprays or low mass loading. But that is the case is Spray CVD so this module could be used in conjunction with the Chemistry, Heat and Flow modules for modelling TCO thin films deposited through Spray CVD. This could greatly increase the understanding of the process and lead to an optimization of the apparatus design in order to achieve the TCO deposit on large area, which is the condition for this method to have really a high potential for industrial application.

5. Summary and conclusion

There has been an increasing effort on the application of numerical methods in recent times. The availability of commercial codes to solve the involved mathematical equations facilitates the numerical analysis in conventional research and production laboratories. In this context, applications to Chemical Vapour Deposition process and equipment are presented with some emphasis to Rapid Thermal CVD by using the CFD'ACE software and some perspectives to exploit this software for modelling Spray CVD.

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