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Wall-Less Like Reactor: Simulation and Experimental Results

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Abstract. The formation of thin films in the conventional thermally activated chemical vapour deposition process is based on heterogeneous reactions involved in surface nucleation and growth. Nevertheless, the influence of homogeneous reactions has often been underestimated, and the intermediate species that are formed from homogeneous reactions may have a great influence on the deposition mechanism. In order to study the formation of these species, a specific reactor has been designed, in which the effects of gas-phase and surface reactions can be separated and so clearly identified. In order to limit the influence of surface phenomena, a so called "wall-less reactor" has been developed. In such a reactor, the reactive gas mixture is heated by mixing with a hot inert gas. Two basic configurations have preliminary been optimized by simulation modelling using the Si-H chemical system. A reactor has been designed according to these calculations. Comparison of the calculated flow pattern with that visualized by the laser sheet method shows an excellent agreement, that partially validates our model. The reactor is coupled with Raman spectroscopy, that allows both the determination of the local temperature of the gas phase and the detection of gaseous species.

1. INTRODUCTION

In standard thermally activated chemical vapour deposition, the films are formed from the heterogeneous reactions of the gas precursors onto the heated surface to be coated. The intermediate species that are formed from homogeneous reactions in the gas phase have a great influence on the deposition process and they can also affect the deposition rate as well as the deposit thickness profile [1-8]. They might also have some influence on the composition and the microstructure of the coatings. The knowledge of the numerous fundamental reaction steps that occur in the gas phase during the CVD process is still rather limited. In order to study the intermediate species formation, a reactor has been designed in which gas-phase and surface reactions can be clearly separated and identified. Our "Wall-Less Reactor" is derived from the so-called reactor developed in 1969 by Taylor in order to limit the influence of surface phenomena during neopentane decomposition or oxygen-ethane reaction [9,10]. In a *wall-less reactor*, the reactive gas mixture is heated by a hot inert gas, the two streams being introduced separately through two concentric tubes in the reactor. Our reactor geometry is an optimization of Taylor's device, performed by numerical simulation. The main differences between the two configurations lie both in heating mode of the inert gas and the inlet position of the gases in the concentric tubes. In the first reactor, the inert gas is introduced through the annular part and the reactive mixture is admitted through the inner tube, the whole reactor being placed in a furnace. In the second one, the inlet of the reactive and inert gases are exchanged and the inert gas is heated by a resistor located in the inner tube which acts as a nozzle.

Our objective was to design a reactor in order to investigate the gas phase reactions by Raman spectroscopy. This spectroscopic method allows both the local temperature determination and the detection of the gaseous species that are Raman active. Due to the low sensitivity of such an analysis, very long lasting measurements are required without perturbation such as solid deposits on the wall of the reactor. For that purpose, it was necessary to fit our reactor with cold observation windows located in the region of the reactor where significant gas phase reactions take place.

The simulation was carried out with our previous simulation model [7,8] and the Si-H chemical system [11]. Simulation results displayed in our previous work [12] have clearly shown that the first configuration is not well fit to spectroscopic analysis for many reasons :

- The domain where the chemical reactions take place is located near the nozzle exit and far from the zone that is investigated by Raman spectroscopy.
- The contribution of the surface phenomena is high, and more than 90% of the initial silicon is converted into silicon deposit.
- Considerable deposition rate, even at the cold window section, would prevent long lasting Raman measurements.

The second configuration was chosen because of its several interesting features that are detailed in part 3, and a device was built accordingly.

The flow patterns were observed by the laser sheet method, with TiO_2 particles as tracer and compared with the results of the simulation. Temperature measurements were performed by Raman spectroscopy using three different methods based on the study of i) the ratio of two pure rotational bands of H_2 ii) the pure rotational bands of N_2 or H_2 (diluted in the carrier N_2 gas). After these preliminary measurements, we checked the method described by Huguet and Gaufrès [13] applied to the fundamental vibrational band of nitrogen (2330 cm^{-1}). These values were compared with the measurements of an aspiration thermocouple that was used to calibrate and to compare with the spectroscopic methods. The first results of the temperature determination are reported.

2. REACTOR CONFIGURATION

Figure 1: Schematic of the favourable configuration

In the most interesting case presented in figure 1, the reactive gas mixture is introduced into the reactor through the annular part at room temperature and the inert gas is heated by a resistance while flowing through the inner tube. The inner diameter of the reactor is 30 mm for a total length of 340 mm. The diameter of the inner tube is 10 mm, and the reactive mixture is admitted into the reactor through a 1 mm width annular section. The two streams are mixed at the exit of the nozzle thus allowing the development of homogeneous reactions. In this cold-wall reactor the observation window can be located at any place along the reactor. Our measurements were carried out at the nozzle exit level which is the hottest zone where the homogeneous reactions take place.

3. SIMULATION DESCRIPTION AND RESULTS

As the results of the modelling were already detailed in our previous work [12], we only review the main results here. As the reactor is disposed parallel to the gravitational field, an axisymmetric 2D model was used. The model included the basic continuity, momentum, energy balance equations and mass balance equation for the species in a diluted system. The numerical integration of the partial differential equations on the elementary volumes formed by the mesh grids was performed by the finite-volume technique developed by Patankar [14]. In a previous paper [8], we have shown that among 17 species that may be present in the gas phase, a mechanism based on a close sub-system including only 8 silicon-carrier species represents

satisfactorily the deposition rate and profile experimentally observed. The same chemical system has been used in this work in order to simulate the influence of the reactor geometry on the development of homogeneous and heterogeneous chemical reactions.

All the calculations were carried out for an atmospheric pressure and a furnace temperature of 1000 K. Simulated results showing the flow pattern, the temperature gradient, the concentration variations of the following species SiH_4 , SiH_2 , H_3SiSiH , Si_2H_6 , Si_2H_2 , H_2SiSiH_2 , Si_3H_8 and H_2 and the deposition rate are gathered in figure 2. On account of the axisymmetry of the reactor, only one semi-plan delimited by the reactor axis is shown for the variation of each quantity. Note that for a better readability the scales were adapted by an increase of the r-direction with respect to the z-direction. The upward flow configuration presented here is the favourable situation to lower the natural convection influence.

Figure 2 : simulation results

The domain which is investigated by Raman spectroscopy is located in the vicinity of the nozzle where chemical reactions take place thus more intermediate species can be expected in this region. A recirculating zone favours the transport of reactive species towards the centre of the reactor, hence promoting its heating and mixing with the hot inert gas as it is clearly seen on the right hand side (RHS) of figure 2a. As shown

in the left hand side (LHS) of figure 2a, the gas temperature decreases rapidly above the reacting zone and stabilizes to a dimensionless value $T=0.7$ corresponding to a temperature of about 790 K.

The main following conclusions can be drawn from the observation of the concentration profiles of the various species presented in figure 2. The initial species SiH_4 (RHS fig 2.b) is rapidly diluted by the inert gas and in to a large extent consumed by the gas-phase reactions. The H_2 concentration (LHS of fig2.e) is increasing continuously in the downstream direction as a product both of gas-phase and surface reactions. The maximum concentration is encountered close to the axis of the nozzle exit for SiH_2 (LHS of fig.2b), and Si_2H_2 (LHS of fig2.d), where the temperature is hot enough to allow their formation. On the other hand, the concentration of Si_2H_6 (RHS of fig2.c) and Si_3H_8 (RHS of fig2.e) increases downstream as a consequence of the thermodynamic stability of these molecules at low temperature. H_2SiSiH_2 (RHS of fig2.d) and H_3SiSiH (LHS of fig2.c) show a particular behavior : their concentration first reach a maximum at the nozzle exit then begin to decrease rapidly downstream before increasing slowly till the top of the reactor.

Deposition rate in the region of the window is very low (fig2.f) and allows long lasting investigations. Surface phenomena are lower than in the previous configuration and the conversion ratio of silane into silicon is reduced to 29%.

This device is technically more difficult to achieve mainly because of the heating mode of the inert gas. Moreover, mass fractions of intermediate species are smaller, that may increase dramatically the recording time of the Raman spectra.

4 EXPERIMENTAL RESULTS

4.1 Reactor description

In accordance with the previous simulated results, an experimental reactor has been designed (Figure 3).

Figure 3: Schematic of the experimental device

The reactor can be divided into two main parts. The first one, presented as the bottom part includes the admission chambers for gases and cooling water. Both gas flows are concentric and the separation between the two flows is realised by a set of 3 concentric copper tubes in which cooling water is circulating from the central part to the outer part in order to prevent the heating of the reactive mixture during its transport towards the reactor inlet. A Kanthal Crusillite heating resistance with a hot zone of 200 mm is disposed in the inner tube. In order to reduce the heat transfers between the cooling water and the resistance, a quartz tube is placed between the two elements. The resistance temperature is regulated by a PID controller through a thermocouple (Nisil) disposed on the reactor axis.

The upper part of the reactor is made of a quartz tube (ED 30 mm). The end part of the reactor is connected to two exits: a vacuum pump and an exhaust at atmospheric pressure.

5.2 Flow visualization

The flow pattern was revealed by the laser sheet method. TiO_2 particles with a diameter of several micrometers were used as optical tracer. They were formed by mixing titanium tetrachloride and vaporized water according to the reaction: $\text{TiCl}_4 + 2 \text{H}_2\text{O} = \text{TiO}_2(\text{s}) + 4 \text{HCl}$. TiCl_4 and H_2O which were introduced separately into the reactor were transported by a N_2 carrier gas. The TiCl_4 and H_2O concentrations were respectively imposed by a dew point evaporator and a bubbler. The water vapor was admitted through the inner tube at room temperature with a flow rate of 20 l/h while the TiCl_4 vapor was introduced through the annular part at the same temperature with a flow rate of 0.5 l/h. The nitrogen flow rates were controlled by mass flow meters (1 Atm and 0°C). The reaction takes place at the exit of the nozzle. The laser sheet was generated by a cylindrical lens disposed on a laser beam produced by an Argon laser on its green mode at the wavelength of 514 nm with a power ranging from 0.2 to 1.0 W. The flow pattern was filmed with a video camera and the pictures were then extracted with Photoshop software. Comparison between the picture and the calculated flow field shows an excellent agreement (figure 4).

Figure 4 : comparison of the visualized (left) and the modellized (right) flow pattern

5.3 Temperature measurements

5.3.1 Raman spectrometer

The local temperature of the gas phase was determined by Raman spectroscopy which is an in-situ non-invasive method. For that purpose, Raman spectra were recorded by the use of a Jobin-Yvon U-1000 double monochromator with a 1 m focal length. Two holographic diffraction gratings with 1800 grooves/mm are moved by a step per step motor. A 100 μm opening width of the entrance slit offered a good compromise between resolution and intensity of the signal. The above described Argon laser was run at a power of about 2 W. The incident beam was filtered before being focused on a point located on the axis of the reactor. The signal was collected by an afocal system composed of two lenses.

The photons are detected by means of a multichannel CCD-detector cooled with liquid nitrogen at a temperature of 140 K. The detector is a matrix of 578*385 22*22 μm^2 elements which corresponds to a total surface of 12.5*8.5 mm^2 . Due to the very low level of the background noise provided with such a detector, no background subtraction was necessary during the acquisition routine. All the Raman spectra were recorded, treated and displayed by the Prism Package software provided by the manufacturer. The acquisition times were 5 min for the rotational spectra and 10 min for the N_2 vibrational spectra.

5.3.2 Determination of the local temperature

Several Raman based methods are available for the temperature measurement of a gas phase. Most classical methods using the Stokes/anti-Stokes ratio of the pure vibrational band could nevertheless not be applied because the anti-Stokes band was too small in the temperature range that was investigated. The spectra of pure rotational anti-Stokes bands of H_2 were also difficult to analyse since their intensities were low.

Temperature can be determined by the intensity of all the pure rotational bands of diatomic molecules like H_2 or N_2 in the Stokes domain. The intensity of a rotational peak resulting from the transition between the initial state J and the final state $J+2$ with the frequency shift $\Delta\nu$ is given by [15,16]:

$$\ln \frac{I_{J \rightarrow J+2}}{\left(\frac{\nu_0 - \varepsilon \Delta\nu}{\nu_0} \right)^4 \cdot S'(J) \cdot f_m(J) \cdot g_m(J)} = \frac{F(J)hc}{kT} + \ln \frac{K'N}{Q_R} \quad (1)$$

where: ν_0 is the incident beam frequency (19435 cm^{-1}), $\Delta\nu$ is expressed in cm^{-1} , $\varepsilon = +1$ for a Stokes line, $S'(J)$ is the Raman line strength for a rigid rotator and is given [17] for pure rotation transitions by

$$S'(J) = \frac{3(J+1)(J+2)}{2(2J+3)},$$

$f_m(J)$ is a correction for the rigid rotator model, $f_m(J) = 1$ for N_2 molecules, $f_m(J) = 1 + 1.9 \times 10^{-3}[J(J+1) + (J+2)(J+3)]$ for H_2 molecules

$g_m(J)$ is the degeneracy of term arising from the nuclear spin factor and its values depend on the studied species. For H_2 we have $g_m(J) = \begin{cases} 1 & \text{for even initial levels} \\ 3 & \text{for odd initial levels} \end{cases}$

$$\text{while for } \text{N}_2, g_m(J) = \begin{cases} 6 & \text{for even initial levels} \\ 3 & \text{for odd initial levels} \end{cases}$$

$F(J)$ corresponds to the energy of the rotational initial level. For H_2 , $F(J) = BJ(J+1)$ with $B = 59.5 \text{ cm}^{-1}$, and for N_2 , $F(J) = BJ(J+1) - DJ^2(J+1)^2$ where $B = 1.99 \text{ cm}^{-1}$ and $D = 5.76 \cdot 10^{-6} \text{ cm}^{-1}$.

h , k are respectively the Planck and Boltzmann constants and c is the light speed (in $\text{cm} \cdot \text{s}^{-1}$), K' is a constant characteristic of the device and the species. N corresponds to the species concentration and Q_R is the rotational partition function.

By plotting the expression (1) as a function of $\frac{F(J)hc}{k}$, a straight line with a slope of $-1/T$ is obtained.

In our example, the rotational spectrum of H_2 consists of four peaks corresponding to the following transitions: $0 \rightarrow 2$ (356 cm^{-1}), $1 \rightarrow 3$ (586 cm^{-1}), $2 \rightarrow 4$ (816 cm^{-1}), $3 \rightarrow 5$ (1036 cm^{-1})

The rotational spectrum of N_2 is more complex and the four first peaks cannot be observed as they are hidden by the very strong Rayleigh scattering band. The peaks $n^\circ 5$ to 10 are also overlapped by the Rayleigh band, but they can be separated from the exciting line. Peaks $n^\circ 5$ to 17 are recorded in the same spectral field.

The second method checked for the temperature determination, was based on the ratio of the measured intensity of two pure rotational peaks recorded at the unknown temperature on the same ratio at a known reference temperature [18]. The temperature is in that case given by :

$$\frac{1}{T} = \frac{1}{T_{ref}} \cdot \frac{k}{[F(J_1) - F(J_2)]hc} \ln \left[\frac{(I_1 / I_2)_{T_{ref}}}{(I_1 / I_2)_T} \right]$$

This method applied to the H_2 rotational peaks for each possible ratio given by the four recordings, showed a good agreement with the results achieved with the former method.

In order to validate these measurements, the gas temperature was also measured by an aspiration thermocouple and the results obtained by that invasive method are plotted in order to built a calibration chart. The results obtained by the ratio method applied to the peaks $1/0$, $3/0$ and $3/1$ and compared with the chart provided by the aspiration thermocouple are presented in figure 5a. The results obtained by the rotational slope method are compared with the calibration chart in figure 5b.

Figure 5: Temperatures measured by ratio method, aspiration thermocouple and rotational method.

Eventually, a third method based on the absolute area of the difference spectrum was checked. This last method has been determined by Gauffrès and Huguet [18,19] to be the most accurate to determine the temperature of the gas phase with a good reproducibility and has been applied to the Raman fundamental vibration band of N_2 at 2330 cm^{-1} . The spectrum of this transition is first recorded at a reference temperature and afterwards at various temperatures. The integrated intensity of the band for each acquisition is calculated within the same integration limits and normalized onto the area of the band recorded at the reference temperature. The reference spectrum is then subtracted from the spectra corresponding to the various temperatures and the absolute areas of the difference spectra are measured and plotted versus temperature in order to provide a chart allowing the determination of unknown temperatures. This accurate method nevertheless requires some care. The whole band to be measured may not be overlapped by a band due to another species and the spectral position as well as the room temperature which alters significantly the spectral response must be reproduced as accurately as possible. However, as the shape of the band is taken into account and not its intensity, the method is valid up to temperatures at which the chemical species under study starts to dissociate.

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