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ON THE KINETICS OF THE CVD OF Si FROM $\text{SiH}_2\text{Cl}_2/\text{H}_2$ AND SiC FROM $\text{CH}_3\text{SiCl}_3/\text{H}_2$
IN A VERTICAL TUBULAR HOT-WALL REACTOR

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Résumé : Les étapes chimiques des dépôts de Si et SiC à partir des précurseurs respectifs DCS/ H_2 et MTS/ H_2 sont déterminées sur la base d'un calcul thermodynamique relatif aux équilibres homogènes. SiCl_2 apparaît comme une espèce intermédiaire fondamentale dans les deux cas. Le calcul de la sursaturation conduit à des valeurs très élevées, particulièrement à basse température. Le calcul des transferts de chaleur, de quantité de mouvement et de masse, réalisés pour le système DCS/ H_2 , est utilisé pour valider le choix de l'ensemble expérimental chambre de dépôt/substrat (réacteur à zone chaude isotherme, géométrie cylindrique). Les variations de la vitesse de dépôt en fonction de l'inverse de la température, du débit et de la pression totale, mettent en évidence des transitions entre des processus de dépôts contrôlés par des réactions de surface, des transferts de masse ou des facteurs thermodynamiques.

Abstract : The chemical steps of the Si and SiC deposition from DCS/ H_2 and MTS/ H_2 respectively, are approached on the basis of a calculation of the homogeneous equilibria. SiCl_2 appears to be a major intermediate species in both cases. Supersaturation is found to be very high particularly at low temperature. A calculation of the heat, momentum and mass transfers performed for the DCS/ H_2 system, is used to validate the choice of the experimental CVD-chamber/substrate assembly (isothermal hot zone reactor, cylindrical geometry). The variations of the deposition rate vs the reciprocal temperature, gas flow rate and total pressure show the occurrence of transitions between CVD processes controlled either by surface reactions, mass transfers or thermodynamic factors.

1 - INTRODUCTION

While the chemical vapour deposition (CVD) of silicon has been widely developed due to a large need in thin films in the microelectronic industry, silicon carbide has been prepared rather as a bulk by solid state techniques for engineering applications. On the basis of its outstanding electrical, thermal and chemical properties, silicon carbide is more and more prepared by CVD as semiconductive film, refractory or oxydation resistant coating.

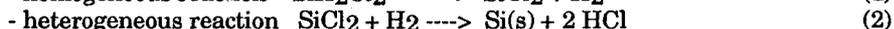
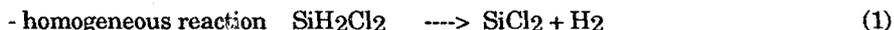
The MTS (methyltrichlorosilane)- H_2 mixture is very often chosen as a gaseous precursor for both economical and theoretical reasons [1]. Although the Si/C ratio equals one in MTS, the stoichiometry of the CVD films can deviate from SiC, i.e. the deposit can be made of Si, C, SiC + Si or SiC + C. As a consequence of the complexity of the Si-C-H-Cl system, the CVD mechanisms which control the kinetic process and the deposit microstructure are not yet known in details.

The aim of this contribution is to show the interest of studies performed (i) on the more simple chemical system Si-H-Cl for the understanding of the CVD of SiC and (ii) with specific CVD geometrical arrangements (in a hot-wall reactor) which permit a good control of the transfer parameters. For both the SiH_2Cl_2 (DCS)/ H_2 and CH_3SiCl_3 (MTS)/ H_2 LPCVD systems, a thermodynamic approach, a calculation of the transport phenomena and an experimental study of the deposition kinetics will be successively presented.

2 - THERMODYNAMIC STUDY

An accurate knowledge of the gas phase composition of a complex chemical system is a first step in the understanding of the kinetic process. The thermodynamic data used for this study were taken from the Scientific Group Thermodata Europe data bank.

The Si-H-Cl system has been widely studied on the basis of both experimental and thermodynamic approaches. In situ or quasi in-situ vapour phase probe techniques such as Raman scattering [2], mass spectrometry [3,4] and infrared absorption spectroscopy [5], have shown that SiCl₂ is among the predominant species in atmospheric pressure reactors. Under reduced pressure conditions, only a few thermodynamic computations were carried out. They led to the conclusion that a decrease of the pressure results in a greater predominance of SiCl₂ and SiCl₄ species at the heterogeneous equilibrium [6-8] (where the condensed phases are not assumed to occur). Another approach suggested to use the homogeneous equilibrium to describe the actual vapour phase within the hot zone of a hot-wall reactor [9]. The following chemical steps have been deduced from this thermodynamic approach :

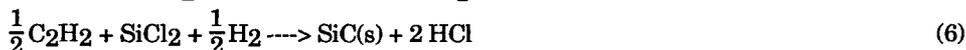
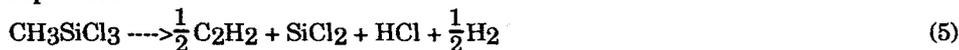


The supersaturation, defined as the gap between the homogeneous equilibrium partial pressures and the heterogeneous ones, was found to be very high (more than 10²), a feature which shows that SiH₂Cl₂/H₂ is an irreversible growth system [9].

The gas phase composition in the Si-C-H-Cl system has not been experimentally studied and the previous thermodynamic approaches were limited to the calculation of the heterogeneous equilibrium for T>1300 K and often P = 1 atm [10-15]. In the present study, homogeneous and heterogeneous equilibria were computed for conditions (i.e. specific initial compositions) which lead thermodynamically to the formation of pure SiC. As shown in figure 1, HCl, SiCl₂ and CH₄ are the predominant species, besides H₂, for both calculations. Furthermore, the partial pressure of CH₄ and SiCl₂ are found to be higher for the homogeneous phase equilibrium than for the heterogeneous one, while it is the opposite for the HCl species. On the basis of these computations, the following reactional process can be proposed for a temperature range around 1200 K, a pressure around 1 kPa and an initial H₂/MTS ratio (α) between 10² and 10⁴ :



For other specific conditions (higher temperatures, lower pressures and lower composition ratios) another carbon intermediate species (C₂H₂) has to be involved in the chemical process of SiC deposition :



The supersaturation, calculated under the previously defined conditions, is found to be higher than 10⁴, a feature which means that MTS/H₂ is a more irreversible growth system than the related DCS/H₂ system, particularly for low values of temperature and pressure (fig. 2). More details on this thermodynamic study will be further published.

3 - MODELLING OF THE TRANSPORT PHENOMENA

Besides the chemical reactions, the physical transfer phenomena (such as diffusion or convection in the vapour phase) can also control the kinetics of the deposition process. The heat, momentum and mass transfers, which have to be modelled, depend on the chemistry of the gaseous mixture, the experimental parameters, but also the reactor and substrate geometry [16,17]. In order to allow a good control and a possible modelling of the transport phenomena, a cylindrical geometry has been theoretically and experimentally chosen for

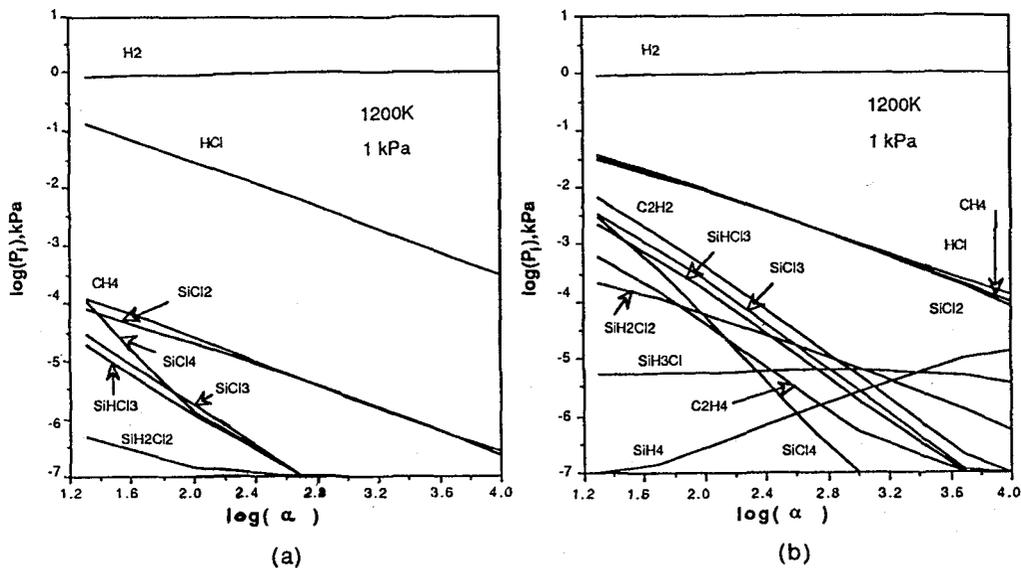


Figure 1: Partial pressures at equilibrium for the Si-C-H-Cl system, as a function of $\alpha = H_2/MTS$ (a) heterogeneous equilibrium, (b) homogeneous equilibrium

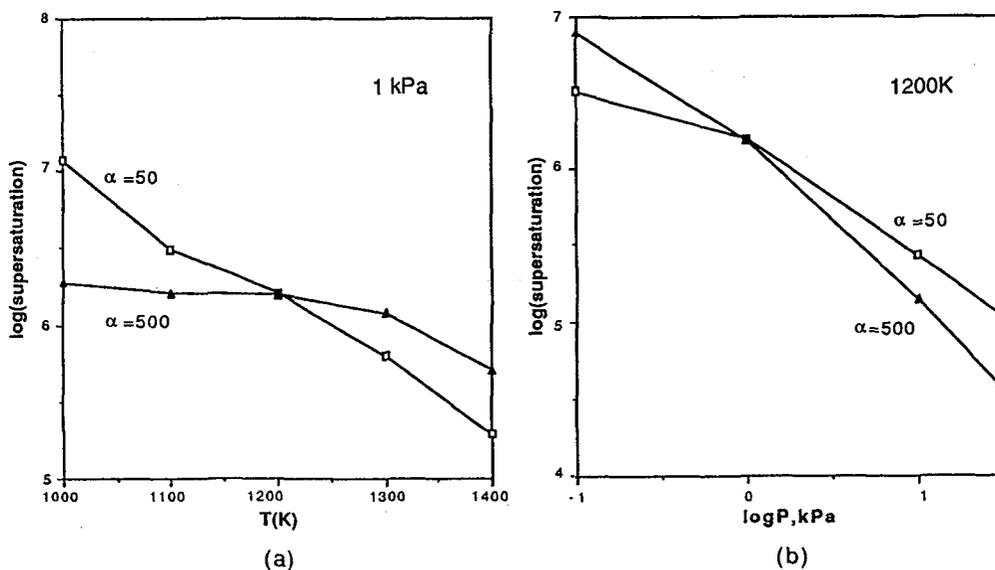


Figure 2 : Variations of the supersaturation as a function of temperature (a) and pressure (b) in the Si-C-H-Cl system

both the hot zone of the reactor and the substrate itself (fig.3). The hot zone is defined by a wall with uniform temperature (graphite susceptor temperature) beyond which it is assumed that temperature is equalled to ambient temperature. As a consequence, the heat and mass transfers are supposed to occur only within this hot reactional area.

3.1 Reynolds number

In a LPCVD reactor, the forced convection flow can be characterized by the Reynolds number Re , defined as a ratio between inertia forces and viscous forces. Re numbers were calculated for both the DCS/H₂ and MTS/H₂ gaseous mixtures under the usual LPCVD conditions. As shown in table 1 the Re values are less than 100 at room temperature, a feature which involves a laminar flow in the cylindrical part of the reactor above the hot zone. This laminar flow is favoured by low total gas flow rates, but also by high H₂ concentrations. It is, on the contrary, rather unfavoured by replacing DCS by MTS. Around the substrate, the Re number is found to be lower than 10, in the hot zone at 1000°C. Thus the laminar flow becomes a creeping flow (table 2) : the gas mixture is flowing down by following the form of the substrate, due to the prevailing viscous forces.

3.2 Heat transfer

The heat transfer occurs by conduction and convection between the hot reactor walls and the gaseous mixture flowing down by laminar forced convection. By solving the heat equation and assuming an axial expansion of the gaseous mixture, the temperature distribution in the reactional area was calculated.

Continuity equation

$$\frac{\partial}{\partial z} \left(\frac{v_z}{T} \right) = 0$$

Heat equation

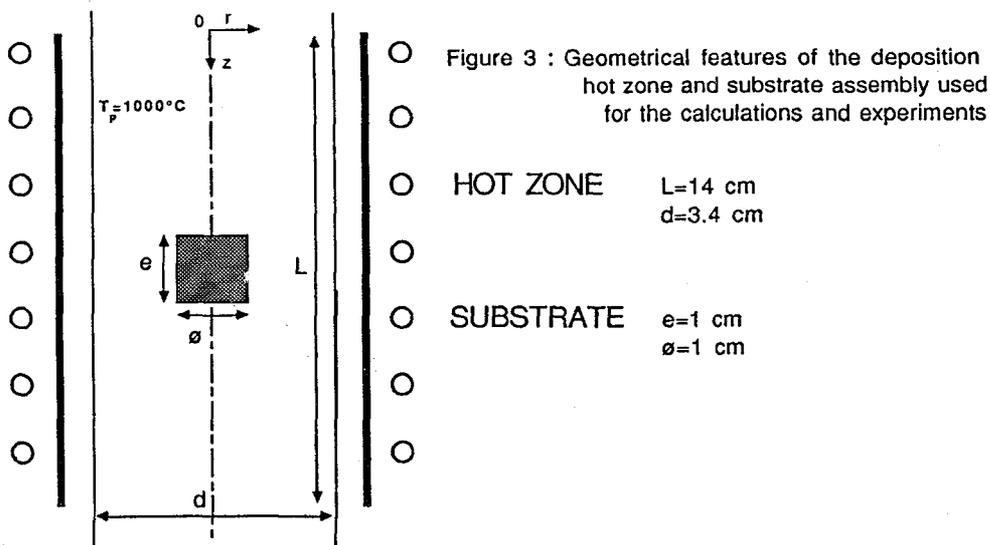
$$\rho C_p v_z \frac{\partial T}{\partial z} = k \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right\}$$

axial convection radial conduction axial conduction

Figure 4 shows a typical example of the radial temperature profiles at various levels in the hot zone, computed for the DCS/H₂ system under classical LPCVD conditions ($T = 1000^\circ\text{C}$, $P = 2 \text{ kPa}$, $Q_{\text{H}_2} = 300 \text{ sccm}$, $Q_{\text{DCS}} = 50 \text{ sccm}$). A large isothermal hot zone is found to extend around the substrate. The size of the hot zone decreases when increasing the total flow rate and the partial flow rate of the source species. The case of MTS/H₂ system is slightly unfavourable to the uniformity of the temperature due to a higher molar mass. However, in most usual conditions, the extent of the isothermal zone is large enough to permit a modelling of the momentum and mass transfers around the substrate without solving the heat equation.

3.3 Momentum transfer

The studied flow was limited to the isothermal zone close to the substrate and assumed to be an axial and radial creeping laminar flow ($Re < 10$). By solving the Navier-Stokes equations and introducing the stream function, a streamline network was drawn, which simulates the actual paths followed by the gaseous mixture (fig. 5).



Q_{DCS} (sccm) \ Q_{H_2} (sccm)	50	100	200	300
50	15.9	16.2	16.8	17.5
100	31.5	31.9	32.5	33.1
200	62.7	63.1	63.6	64.3

(a) DCS/H₂ mixtures

Q_{MTS} (sccm) \ Q_{H_2} (sccm)	50	100	200	300
50	23.5	23.8	24.4	25.1
100	46.7	47.0	47.6	48.2
200	93	93.4	94	94.6

(b) MTS/H₂ mixtures

Table 1: Re numbers for flowing mixtures of DCS/H₂ (a) and MTS/H₂ (b) at 25°C for the cylindrical reactor

Q_{DCS} (sccm) \ Q_{H_2} (sccm)	50	100	200	300
50	1.8	1.9	1.9	2.0
100	3.5	3.6	3.7	3.8
200	7.1	7.2	7.2	7.3

(a) DCS/H₂ mixtures

Q_{MTS} (sccm) \ Q_{H_2} (sccm)	50	100	200	300
50	2.7	2.7	2.8	2.9
100	5.3	5.4	5.4	5.5
200	10.2	10.5	10.7	10.8

(b) MTS/H₂ mixtures

Table 2 : Re numbers for flowing mixtures of DCS/H₂ (a) and MTS/H₂ (b) around the substrate in the isothermal hot zone (1000°C) of the cylindrical reactor

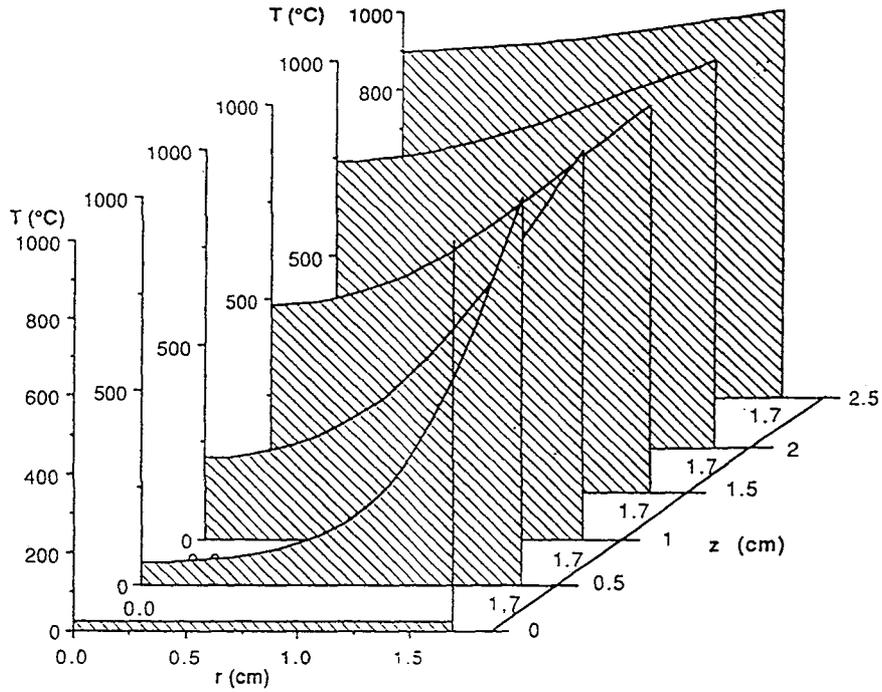


Figure 4 : Typical temperature radial profiles in different cross sections of the hot zone for the cylindrical CVD reactor shown in fig.3

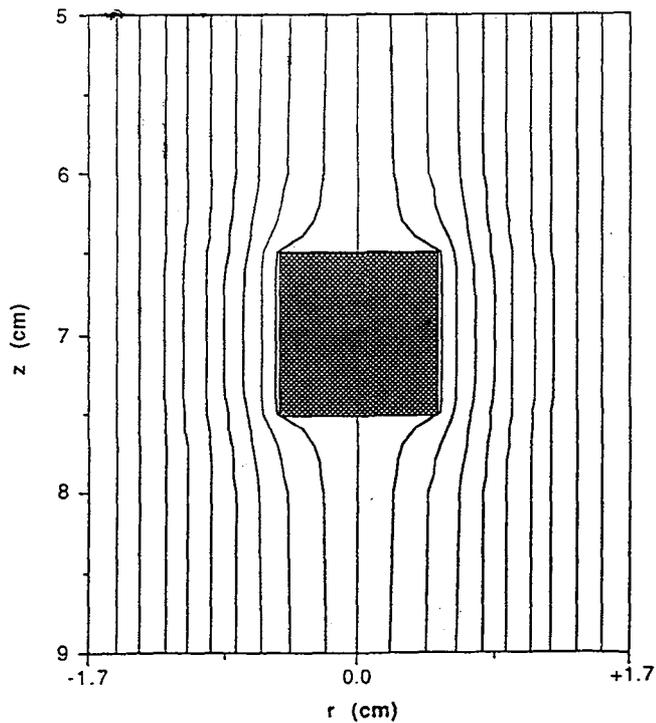


Figure 5 : Streamlines for the cylindrical substrate/reactor assembly shown in fig.3

Navier-Stokes equation

$$\begin{aligned} \text{Streamline function } \psi \quad v_r &= \frac{1}{r} \frac{\partial \psi}{\partial z} \\ v_z &= -\frac{1}{r} \frac{\partial \psi}{\partial r} \end{aligned}$$

$$\text{Creeping laminar flow } \Rightarrow \quad E^4 \psi = 0$$

$$\text{with } E^2 \psi = -\frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial z^2}$$

The only flow disturbance was found to take place very close to the base surface of the substrate where a radial component of the velocity occurs. In the annular zone between the substrate and the reactor wall, the calculation gave an axial flow with an increase in the gas phase velocity and narrower streamlines. The gas flow is not much disturbed by the occurrence of the substrate, due to the creeping flow. Under this hypothesis, when inertia forces are negligible with respect to viscous forces, the Navier-Stokes equations can be reduced to one equation which does not include the viscosity [16]. Consequently, the velocity field in the reactional zone does not depend on the composition of the gas phase (with the same result for both DCS/H₂ and MTS/H₂ systems) unless the Reynolds number is too much increased.

3.4 Mass transfer

The mass transfer study, which implies a good knowledge of the chemical system, was carried out on the DCS/H₂ system under the following hypotheses (partly based on the previous thermodynamic results) :

- total and instantaneous homogeneous decomposition of SiH₂Cl₂ at the entrance of the hot zone : reaction(1)
- heterogeneous reaction : reaction (2)
- kinetic limiting step : axial and radial mass transfer by convection and diffusion.

As consequences of these assumptions :(i) there is no production of chemical species by homogeneous reaction within the bulk of the hot gaseous phase, (ii) SiCl₂ is considered as the only source species going towards the solid surfaces (substrate and reactor wall) and (iii) its concentration at these surfaces is zero due to its instantaneous consumption by the heterogeneous reaction.

By solving the continuity equation for the SiCl₂ species and using the axial and radial velocity profiles previously determined, the SiCl₂ molar fraction distribution was calculated in the hot zone around the substrate.

Continuity equation

$$v_r \frac{\partial y_i}{\partial r} + v_z \frac{\partial y_i}{\partial z} = D_{im} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial y_i}{\partial r} \right) + \frac{\partial^2 y_i}{\partial z^2} \right\}$$

radial convection axial convection radial diffusion axial diffusion

When the mass transfer is the limiting step of the kinetic process(i.e. for T = 1050°C, P = 2 kPa, Q_{H₂} = 210 sccm and Q_{DCS} = 7 sccm as it will be shown further), the SiCl₂

concentration was found to decrease as the gaseous phase is flowing down in the reactor (fig.6)

On the basis of this model, the deposit thickness on the substrate surface was calculated and found to be rather heterogeneous as shown in figure 7. This result, which has to be confirmed experimentally, can be explained on the basis of gas flow velocity values at the substrate edges and rapid depletion of the SiCl_2 reactant species along the reactor axis. Analogous thickness profiles were recently obtained for a stagnation flow reactor [18].

In the case of the MTS/ H_2 system, the modelling which is still in progress is based on the transfer of both SiCl_2 and CH_4 for given specific conditions. The complexity of the treatment is increased due to the production of gaseous molecules involved by the stoichiometry of the heterogeneous deposition reaction.

4 - EXPERIMENTAL STUDY OF THE KINETICS

The respective contributions of the physical and chemical steps involved in the CVD process to the kinetics of deposition has to be investigated on the basis of an experimental approach. The measurements of the growth rates were carried out in-situ by a continuous recording of the sample mass with a microbalance connected to a microcomputer.

4.1 Temperature dependence

For both DCS/ H_2 and MTS/ H_2 systems, the growth rate is plotted in figure 8 as a function of the reciprocal temperature for various values of the composition ratio α (PH_2/PDCS or PH_2/PMTS).

The Arrhenius plots exhibit a rather similar behaviour in the low temperature range ($T \leq 850^\circ\text{C}$) where an activation energy of about $40 \text{ kcal mole}^{-1}$ can be determined. This value is in accordance with results already published for the deposition of silicon from DCS/ H_2 [19-21]. For the MTS/ H_2 system the occurrence of elemental silicon in the deposit has been established from analyses by X-ray diffraction and Raman spectroscopy within this temperature range. Thus, the limiting step of the kinetic process seems to be in both systems the heterogeneous reaction (2).

For higher temperatures, the thermal variations of the deposition rate obey more complex laws with similar ($850 < T < 1050^\circ\text{C}$) or different ($T > 1050^\circ\text{C}$) features. Mass transfer phenomena which are slightly thermally activated and exothermic chemical processes such as reaction (6) and to a less extent reaction (2), might be taken into account as limiting step in the overall CVD mechanism.

4.2 Total flow rate dependence

The variations of the growth rate versus the total flow rate are drawn in figure 9-a for the DCS/ H_2 system. At $T=850^\circ\text{C}$ and $P=2$ or 5 kPa the growth rate is characterized by rather low values which do not depend on the total flow rate : this result confirms the previous conclusion of kinetic process controlled by a surface chemical reaction (probably reaction (2)) at low enough temperatures. At 1000°C and 2 kPa , the deposition rate increases with the total flow rate, a feature which means that the CVD process may be limited by the diffusion transport of reactant species (probably SiCl_2) through a boundary layer whose thickness decreases as the total flow rate increases. For the same temperature and a lower pressure of 1 kPa , a transition induced by the total flow rate is evidenced between both mechanisms.

The thermal variations of the growth rate in the MTS/ H_2 system are shown in figure 9-b for temperatures higher than 1000°C where a pure SiC deposition is obtained. The kinetic process seems to remain controlled by transport phenomena in the whole flow rate range which was limited to 130 sccm because of technical reasons concerning the bubbling

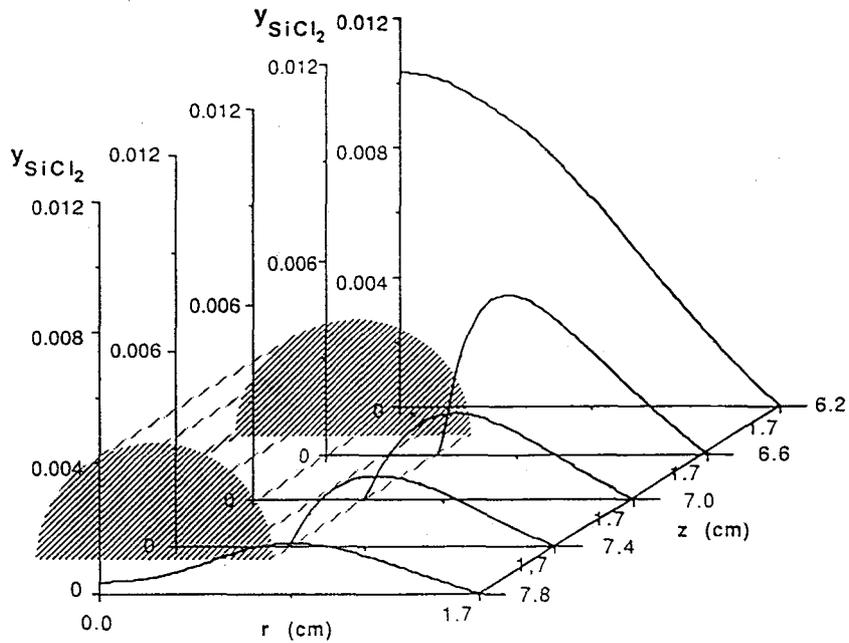


Figure 6: Computed radial variations of the SiCl_2 molar fraction in various cross sections of the gas phase near the substrate, for the cylindrical substrate/reactor assembly shown in fig.3

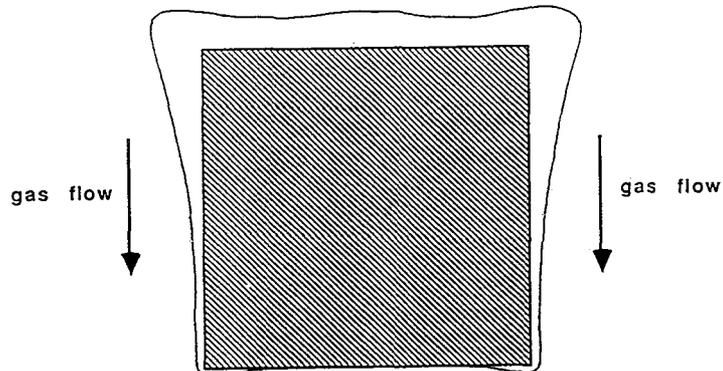


Figure 7 : Calculated thickness profile of a silicon deposit on the cylindrical substrate shown in fig.3, for a deposition process rate-limited by mass transfer

$$\begin{aligned}
 T &= 1050^\circ\text{C} \\
 P &= 2.2\text{kPa} \\
 Q_{\text{H}_2} &= 300\text{sccm} \\
 Q_{\text{DCS}} &= 10\text{sccm}
 \end{aligned}$$

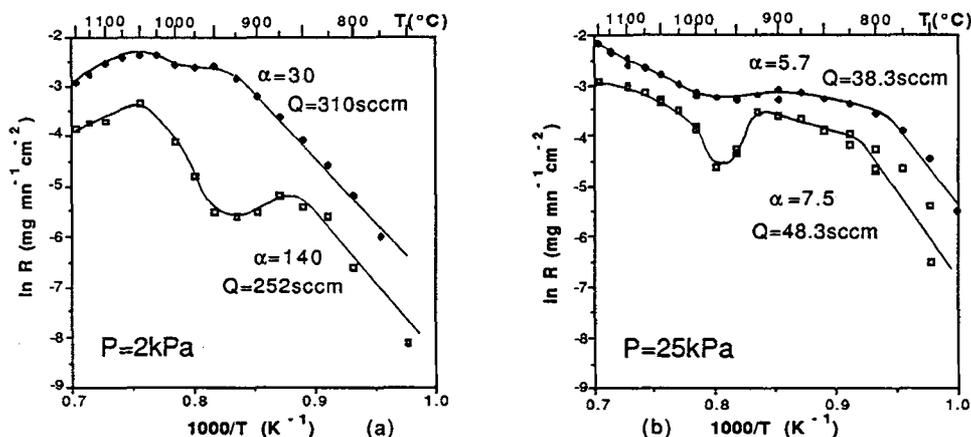


Figure 8: Arrhenius plots of the thermal variations of the deposition rate for (a) the DCS/ H_2 system and (b) the MTS/ H_2 system

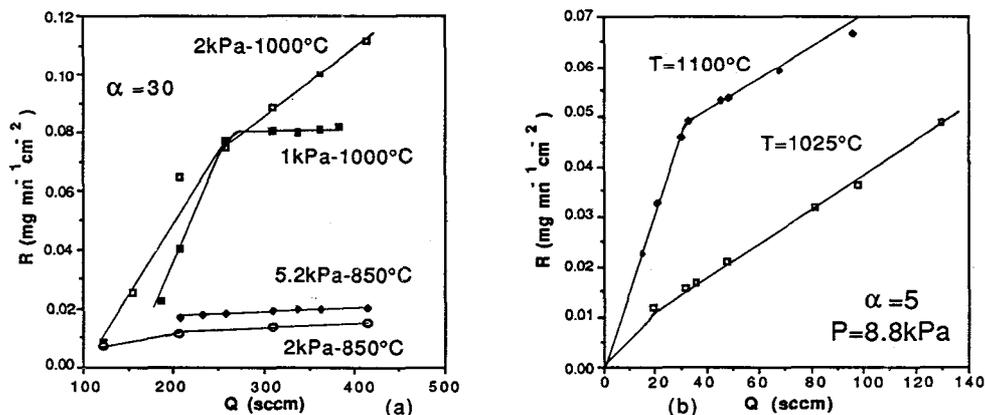


Figure 9: Variations of the deposition rate with the total gas flow rate for (a) the DCS/ H_2 system and (b) the MTS/ H_2 system

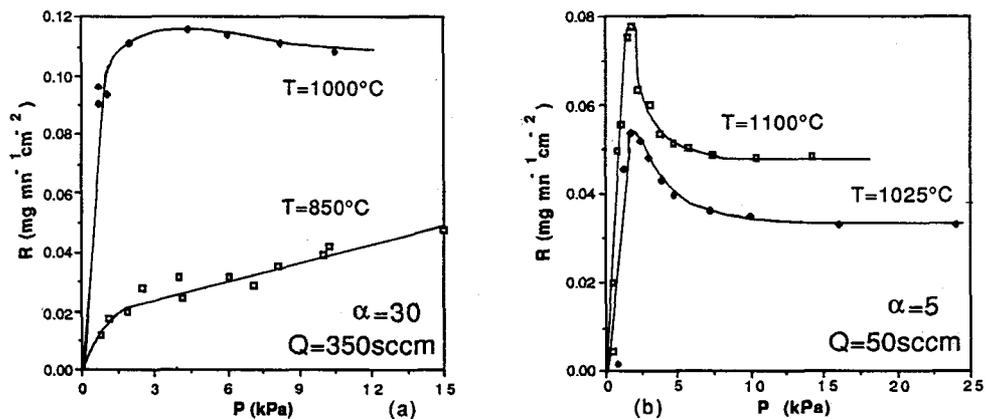


Figure 10: Variations of the deposition rate with the total pressure for (a) the DCS/ H_2 system and (b) the MTS/ H_2 system

system of H₂ in liquid MTS. The surface reaction control should occur for higher flow rates and lower temperatures.

4.3 Total pressure dependence

The influence of the total pressure on the Si(DCS/H₂) and SiC(MTS/H₂) deposition rate is presented in figure 10.

For T = 850°C, the surface reaction control of the Si CVD process seems to be confirmed again by the increase of the growth rate with pressure. At 1000°C, two pressure ranges are observed : (i) below 2kPa, the Si deposition rate increases rapidly with pressure (control by a chemical reaction) and (ii) above this value, it remains almost constant, a feature which means either a control by a chemical reaction with an overall zero order or a control by diffusion phenomena.

In the MTS/H₂ system, the thermal variations of the SiC deposition rate drawn at temperatures higher than 1000°C exhibit a similar transition induced by pressure with a marked maximum between both mechanisms.

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