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Kinetic Processes in the CVD of SiC from $\text{CH}_3\text{SiCl}_3\text{-H}_2$ in a Vertical Hot-Wall Reactor

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Abstract : The chemical vapour deposition of SiC-based ceramics from the $\text{CH}_3\text{SiCl}_3\text{-H}_2$ precursor is investigated on the basis of large scale experimental and theoretical approaches. The use of a vertical cylindrical hot-wall LPCVD reactor permits to get a wide isothermal reaction zone with a creeping laminar flow around the substrate and a largely chemical control of the kinetics, which favours a high supersaturation and a nucleation regime. A calculation of the coverage of C(111) or Si(111) planes of SiC points out the importance of the chemisorption of SiCl_3 and H radicals on C atoms and of CH_3 and Cl radicals on Si atoms. On the basis of kinetic experiments and of chemical and structural investigations of the deposits, several domains of conditions are defined with different mechanisms for the formation of SiC-based ceramics. For low temperatures and low pressures, a regime of growth of stoichiometric SiC microcrystals occurs from reaction of CH_3 and SiCl_3 intermediates. Higher pressures in the chemical control kinetic domain, favour a regime of nucleation of nanocrystals with an excess of silicon resulting from $\text{SiCl}_3/\text{SiCl}_2$ effective silicon precursor.

1- INTRODUCTION

In both main application fields of silicon carbide obtained by CVD/CVI, i.e. ceramic matrix composites and electronic devices, a good knowledge of the physical and chemical mechanisms involved in the synthesis process is needed to control and possibly improve the characteristics of these materials, such as mechanical and electronic properties [1].

The purpose of the present paper is to show the interest of using simultaneously various theoretical and experimental approaches in the investigation of CVD process, particularly in the case of CH_3SiCl_3 (MTS)/ H_2 systems used for the synthesis of SiC matrix composite materials. A theoretical study of the transport phenomena has first permitted to justify the choice of the reactor. On the basis of a thermodynamic study of both the homogeneous and heterogeneous equilibria, the supersaturation of the gas phase and the composition of the adsorbed layer on SiC were assessed and correlated to nucleation experiments. An experimental study of the growth rate was also carried out in order to derive the various kinetic control regimes and the corresponding kinetic laws. Chemical and structural properties of the SiC-based deposits have been investigated from a micro- to a nanometric scale and correlated to the kinetic regime of the deposition process. By taking into account the results of these various approaches, homogeneous and heterogeneous reactional mechanisms are finally discussed.

2- EXPERIMENTAL AND MASS TRANSPORT

The first step in the present investigation was the choice of the CVD reactor : it is vertical, cylindrical, with hot walls and it works under reduced pressure. The experimental set-up is presented in figure 1. The

studied conditions are the following : $800 \leq T \leq 1100^\circ\text{C}$ for the temperature, $1 \leq P \leq 50$ kPa for the total pressure, $1 \leq \alpha \leq 10$ for the dilution ratio $P(\text{H}_2)/P(\text{MTS})$ and $10 \leq Q \leq 500$ sccm (standard cubic centimeter per minute) for the total flow rate.

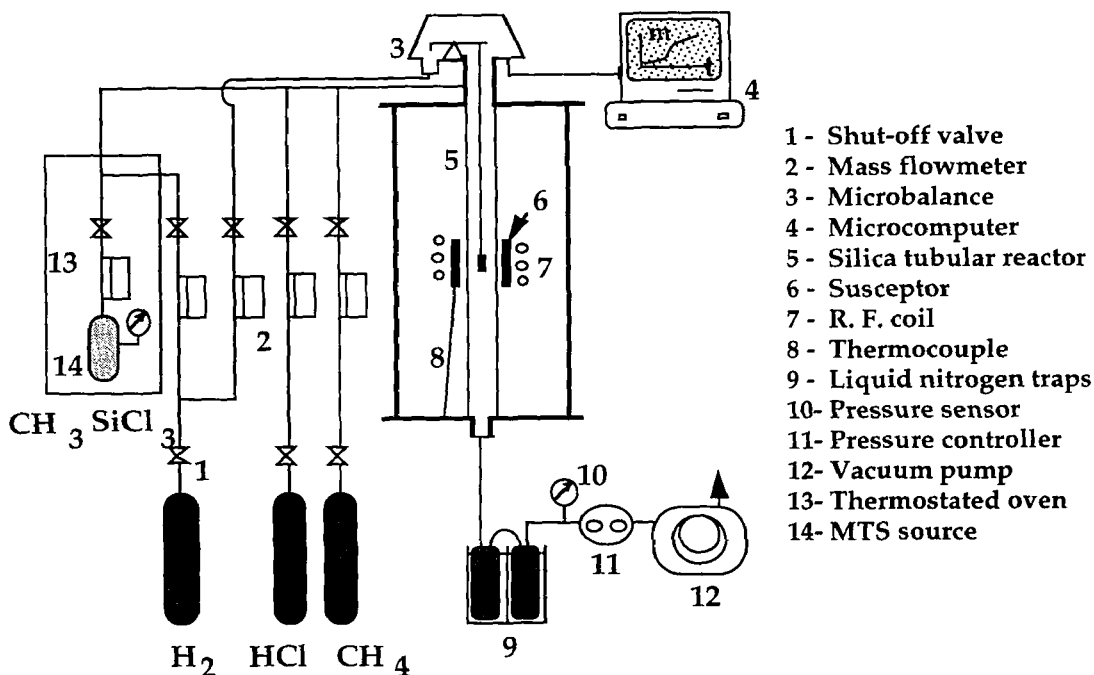


Figure 1: Schematics of the CVD equipment

The vertical reactor is coupled to a microbalance (sensitivity of $2.5 \mu\text{g}$) permitting in-situ measurements of the deposition rate as a function of experimental conditions.

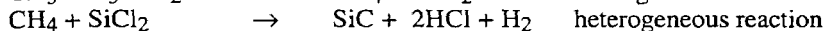
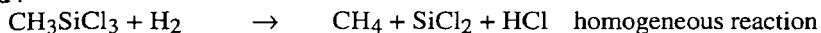
The choice of hot walls can be justified by calculating the conductive and convective heat transport between the reactor walls and the gaseous mixture flowing down by forced convection. Solving the heat equation, the temperature distribution in the reactional area was calculated and a large isothermal hot zone was found to extend around the substrate [2], which results in a residence time mostly higher than 0.1 s.

The cylindrical geometry of both the reactor and the substrate can be justified by studying the forced convection flow (momentum transport). The Reynolds number was found to be lower than 10 in the hot zone around the substrate, corresponding to a creeping laminar flow [2]. By solving the Navier-Stokes equations, the calculation of the gas velocities and the streamlines has shown that the gas flow is not much disturbed by the occurrence of the substrate.

By modelling the momentum and mass transfer, the concentration fields and the layer thickness profiles were calculated. The results show that the physically limited growth rate is not influenced by total pressure, hardly by temperature and is increased by increasing the total flow-rate [3]. On the other hand, the chemical reaction rate is enhanced by increasing the total pressure. As a consequence, reduced pressure conditions (i.e. $P < 100$ kPa) were chosen favouring an overall process controlled by the rate of chemical reaction and in most cases leading to relatively homogeneous deposits [4].

3- APPROACHES BASED ON THERMODYNAMICS

A thermodynamic study of the Si-C-H-Cl system, including the calculation of the heterogeneous and homogeneous equilibria, has permitted to show that in a hot wall reactor, the precursor molecule MTS is not the actual source species, but is decomposed to two intermediate species SiCl_2 and CH_4 , respective source species for silicon and carbon in the most general case (fig. 2). The following reactional process is derived :



With increasing molar fraction of the MTS and temperature and with decreasing total pressure, the importance of C_2H_2 as a carbon source increases and the importance of CH_4 decreases [5].

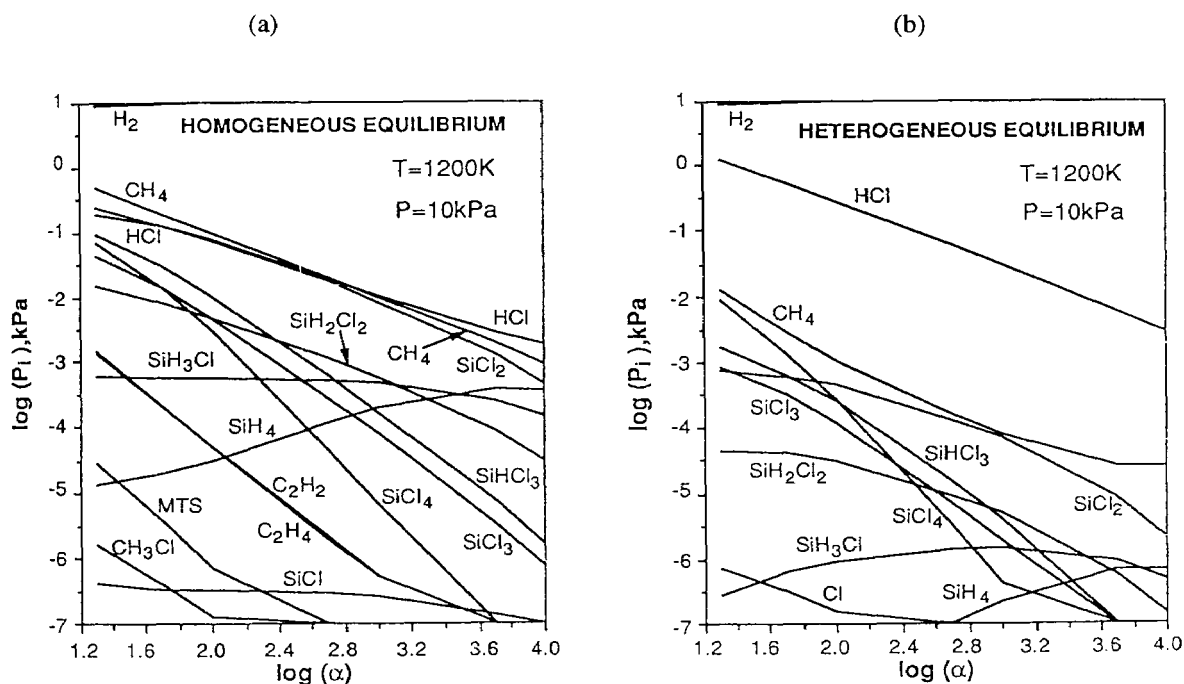


Figure 2: Partial pressures of the gaseous species versus α at 1200K and 10kPa in the hypothesis of (a) homogeneous equilibrium and (b) heterogeneous equilibrium of the Si-C-H-Cl system.

Partially based on these thermodynamic calculations, the supersaturation of the gas phase, which represents the difference between the actual state and the equilibrium, was evaluated and correlated to the nucleation of SiC, which corresponds to the first instants of the deposition [6]. The nucleation studies were performed using silica substrates to determine the density of nuclei as a function time (fig. 3). From these data, the nucleation rate, the saturation nucleus density (i.e. corresponding to the maximum of nucleus density) and the saturation nucleus size were derived. For relatively low temperatures, low total pressures and more generally for an overall process controlled by the kinetics of the surface reactions, (e.g. for a temperature around 900°C and a total pressure of about 3 kPa), the supersaturation of the gas phase close to the substrate, assessed by the ratio between homogeneous and heterogeneous partial pressures, is found to

be higher than 10^5 . Under these conditions, the nucleation rate and the saturation nucleus density are relatively high (respectively about $10^{13} \text{ m}^{-2} \text{ s}^{-1}$ and 10^{14} m^{-2}), the saturation nucleus size is relatively low (about 10 nm) and a rapid continuous nucleation seems to be favoured by a very high local supersaturation. Under conditions of higher temperatures, higher total pressures and more generally of an overall process controlled by the kinetics of mass transport (e.g. for $T \approx 1100^\circ\text{C}$ and $P \approx 20 \text{ kPa}$) the local supersaturation cannot be calculated without a good knowledge of the boundary layer, but can be assumed to be rather low, due to local partial pressures approximately given by the heterogeneous equilibrium. In this case, the nucleation rate and the saturation nucleus density are lower (respectively about $10^{11} \text{ m}^{-2} \text{ s}^{-1}$ and 10^{12} m^{-2}), the saturation nucleus size is higher (about 100 nm) and a growth regime instead of a nucleation process seems to be favoured by a very low local supersaturation.

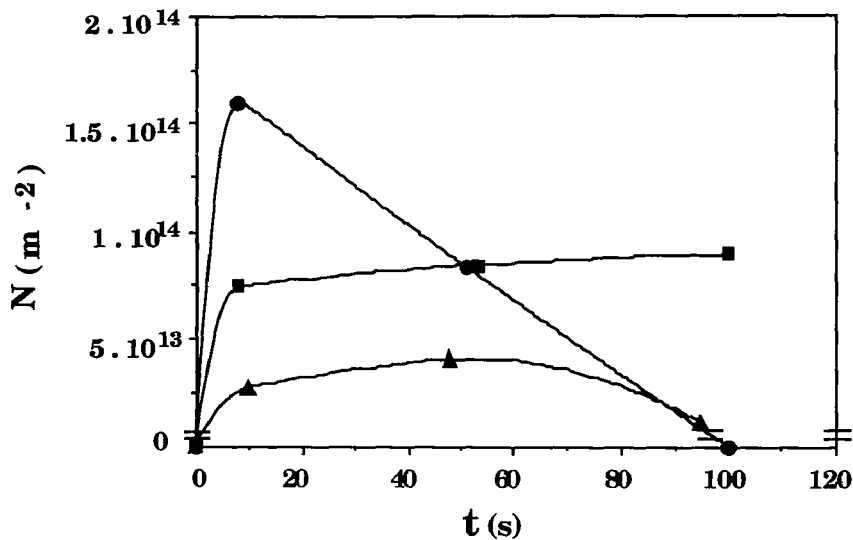


Figure 3 : Variations of the nucleus density versus deposition time for the following CVD conditions:

■	T = 900°C	●	T = 900°C	▲	T = 1100°C
	$\alpha = 30$		$\alpha = 3$		$\alpha = 30$
	P = 20kPa		P = 3kPa		P = 3kPa
	Q = 200 sccm		Q = 200 sccm		Q = 200 sccm

The thermodynamic approach is also needed to estimate the concentrations of various chemical species chemisorbed on SiO_2 or $\beta\text{-SiC}$ surfaces. This theoretical study of chemisorption in the Si-C-H-Cl system, was carried out to understand experimental SiC nucleation and growth on various substrates. On the basis of the Langmuir model, the assessment of the chemisorbed layer giving the coverages θ_i of the various species [7] on (i) an oxygen atoms surface (SiO_2 substrate) and (ii) a surface made of alternately carbon and silicon atoms ($\beta\text{-SiC}$ substrate), has pointed out the major occurrence of (i) radical H on SiO_2 (fig. 4 a) and on a C(111) plane of $\beta\text{-SiC}$ (fig. 4 c) and (ii) radical Cl on a Si (111) plane of $\beta\text{-SiC}$ (fig. 4 b). In this way, the main source species playing a role in the SiC growth by their chemisorption, have been identified: SiCl_3 and Si on the C surface, C_2H_2 and CH_3 on the Si surface. Nucleation experiments carried out on both SiO_2 and $\beta\text{-SiC}$ have evidenced some selectivity of the deposition with respect to the nature of the substrate surface, which results in a preferred growth on $\beta\text{-SiC}$. This can be correlated to an important poisoning of the SiO_2 surface by H radicals instead of the favorable chemisorption of source species.

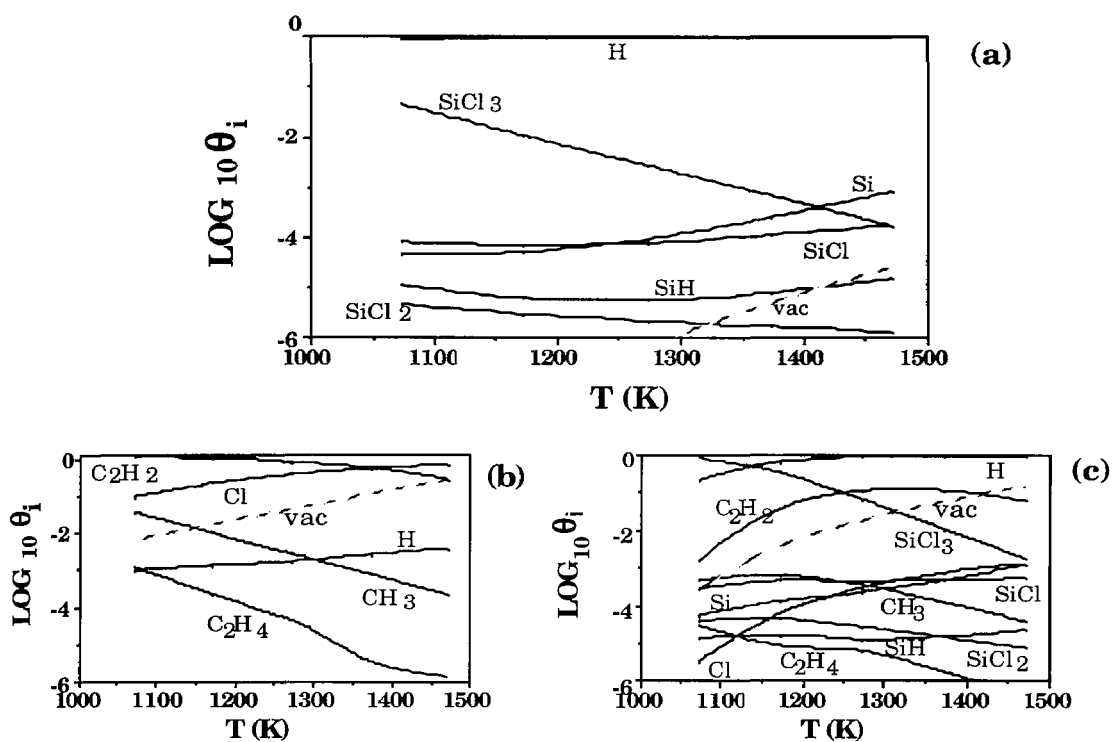


Figure 4: Coverages of (a) a SiO_2 surface, (b) a Si (111) plane of $\beta\text{-SiC}$ and (c) a C (111) plane of $\beta\text{-SiC}$ (under homogeneous equilibrium assumption) as a function of temperature T for $\alpha=1$ and $P=1\text{kPa}$

4- EXPERIMENTAL KINETICS

A preliminary study of the MTS decomposition by using Mass Spectrometry at the outlet of the reactor has shown that MTS is not totally decomposed under the studied conditions of T , P and α , unlike predicted by the thermodynamic calculations. This homogeneous decomposition is favoured by increasing temperature and total pressure. Its activation energy is about 350 kJ mol^{-1} for $\alpha = 5$ and $1 \leq P \leq 10\text{ kPa}$ [8].

The heterogeneous kinetics of SiC deposition was investigated by studying the variations of the growth rate with the various experimental parameters T , P , Q and partial pressures of MTS, H_2 and HCl . For $3 \leq \alpha \leq 10$, kinetic $P - T$ diagrams were established defining the various regions of mass transport regime (MTR) and of chemical reaction regime (CRR) (fig. 5). The transition from CRR to MTR domain is induced by increasing temperature and, to a lesser extent, by increasing total pressure. The CRR region can be divided into three sub-domains. CRR1, for low temperatures ($T \approx 800^\circ\text{C}$) and low pressures ($P \leq 10\text{ kPa}$), is characterized by a very high activation energy ($E_a > 500\text{ kJ mol}^{-1}$) and a reaction order of 2 with respect to MTS : the rate of the overall process is limited by both the homogeneous MTS decomposition and the surface reactions. CRR2, for a medium temperature ($T \approx 900^\circ\text{C}$) and a large range of pressure ($1 \leq P \leq 30\text{ kPa}$), is characterized by an activation energy of about 190 kJ mol^{-1} and a reaction order with respect to MTS of 0 at low pressure [9] and 1 at high pressure [10] : kinetics is only limited by heterogeneous reactions. The third sub-domain CRR3, whose size is limited in temperature ($950 \leq T \leq 1025^\circ\text{C}$) and pressure ($5 \leq P \leq 15\text{ kPa}$), is characterized by a marked change of the growth rate and of the activation energy [11].

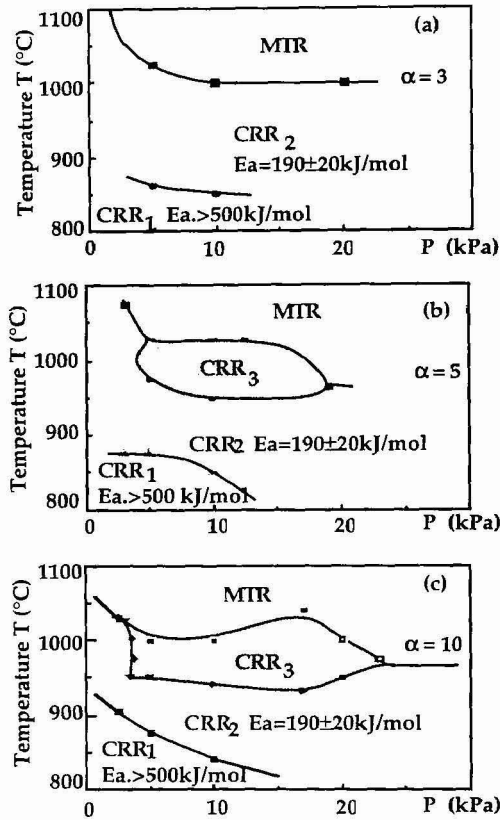


Figure 5: Temperature-pressure kinetic control diagram established for Q=200sccm

5- CHEMICAL AND STRUCTURAL PROPERTIES OF THE DEPOSITS

For each kinetically defined domain or sub-domain , the deposits were characterized in terms of morphology, structure, nano-structure and chemical composition using various techniques such as scanning electronic microscopy (SEM), transmission electronic microscopy (TEM) and electron energy loss spectroscopy (EELS) [12].

In the MTR domain, the surface morphology of the deposits is angular and rough. The layer consists of microcrystalline columnar stoichiometric SiC-grains, the main growth direction <111> of which is perpendicular to the substrate (fig. 6).

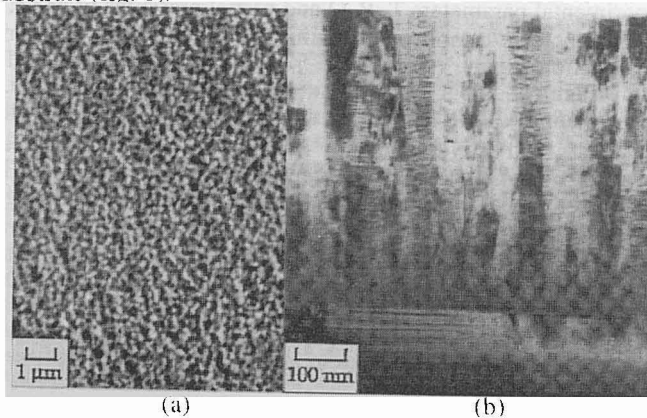


Figure 6: (a) Surface morphology (SEM) and (b) cross-section microstructure (TEM bright field image) of the deposit in the MTR domain

In the CRR domain, the physico-chemical characteristics of the deposits depend on the total pressure. At relatively low pressure ($P \approx 5$ kPa), the surface morphology is rough. The crystallites have a columnar-like shape but the growth axis is no longer exactly perpendicular to the substrate surface as for the MTR deposits. The crystallite size, measured from the columnar width on TEM bright-field images, is about 100 nm (fig. 7 a). The deposits are stoichiometric or present a slight silicon excess (Si/SiC ratio ≈ 0.3). At higher pressures ($P > 10$ kPa) in the same CRR domain, the deposits exhibit a smooth surface morphology, a nanocrystallized structure and a silicon excess with Si/SiC ratio ranging from 1.5 to 3 (fig. 7 b).

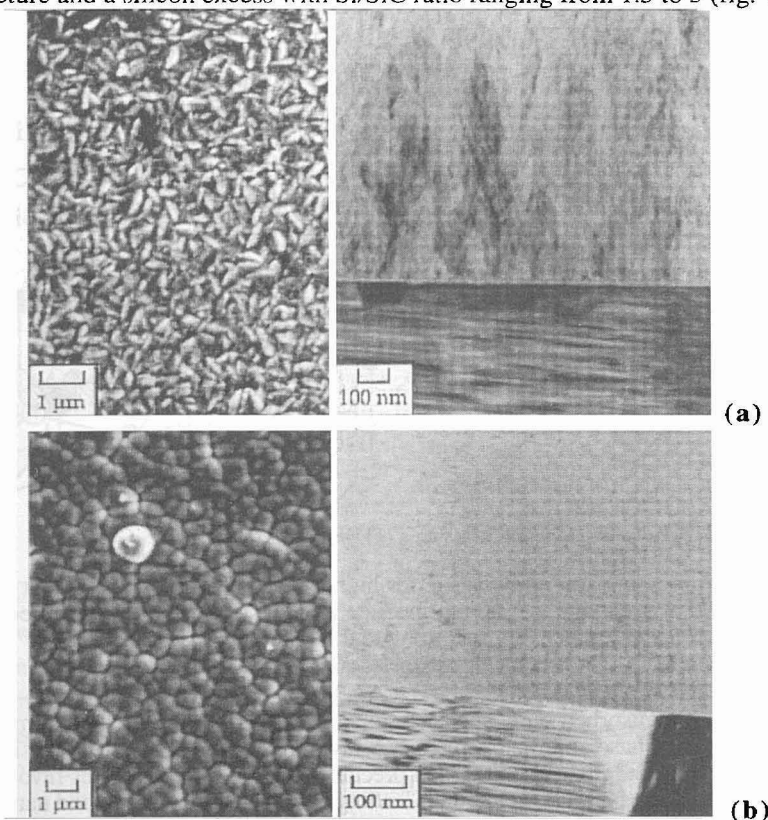


Figure 7: Surface and cross-section structure of the deposit in the CRR domain for $T=925^{\circ}\text{C}$, $\alpha=5$ and (a) $P=5\text{kPa}$, (b) $P=19\text{kPa}$

In the CRR3 sub-domain, characteristics of the deposits are intermediate between those identified for the regions CRR2/low pressure and CRR2/high pressure.

6- DISCUSSION

On the basis of these various theoretical and experimental approaches, different mechanisms can be proposed for the deposition of SiC-based ceramics from $\text{CH}_3\text{SiCl}_3\text{-H}_2$ precursor.

In the sub-domains CRR1 and CRR2/low pressure, i.e. at low temperature and low residence time, the extent of the homogeneous decomposition of MTS is very small and the only reactive species are CH_3 and SiCl_3 radicals, resulting from the breaking of the weakest bond in MTS : Si-C [13,14]. As shown in the chemisorption study, CH_3 can be largely adsorbed on Si atoms and SiCl_3 on C atoms. During the growth of stoichiometric $\beta\text{-SiC}$ crystals in the $\langle 111 \rangle$ direction, the surface can include (i) (111) Si atomic planes whose tetrahedral Si atoms have one dangling bonds perpendicular to the surface and (ii) step ledges whose C atoms have one or two lateral dangling bonds (fig. 8). The growth can go on according to two successive heterogeneous steps : the chemisorption of CH_3 and SiCl_3 without breaking the tetrahedral structure of the solid followed by the reaction between chemisorbed species, i.e. the evolution of HCl by cooperative breaking of Si-Cl and C-H bonds. The dissociation of HCl into H and Cl radicals is very low but the adsorption of H on C surface atoms and of Cl on Si are very easy, which can compete with the adsorption

of SiCl_3 and CH_3 resulting in a possible inhibition effect. Nevertheless, under conditions of low temperature and low pressure, this inhibition is very small because the surface is not saturated with reactive species and then diffusion towards stable growth sites is easy, which favours a regime of growth of stoichiometric β -SiC microcrystals.

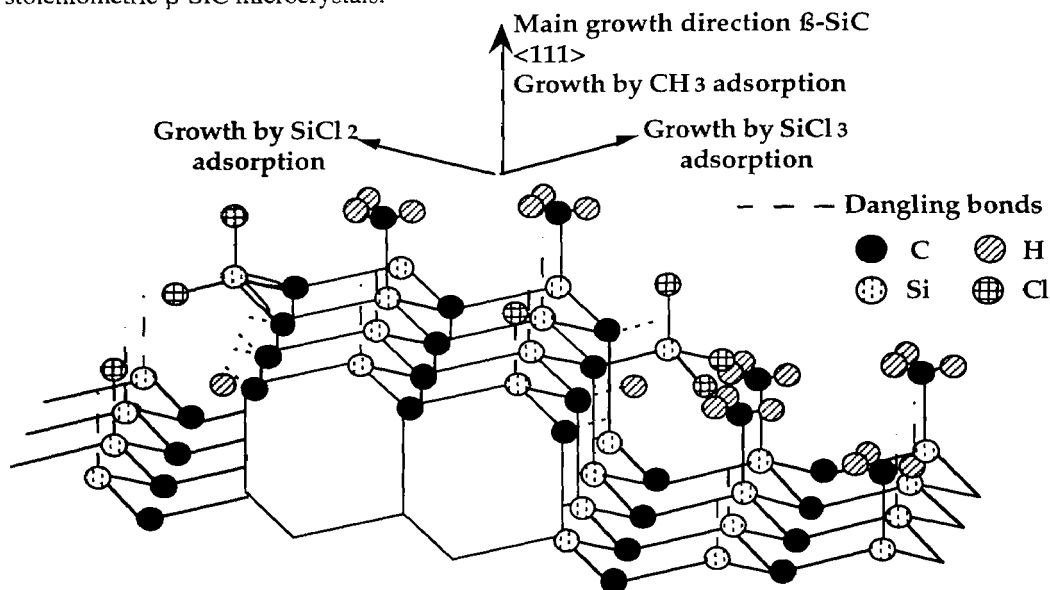
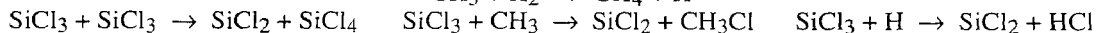
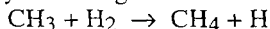


Figure 8: Growth process on a (111)Si atomic plane of β -SiC

In the CRR2/high pressure sub-domain, i.e. for higher residence times, the extent of the homogeneous decomposition of MTS is enhanced, the intermediate radicals CH_3 and SiCl_3 formed in the first step are converted to CH_4 and SiCl_2 respectively according to the following reactions [15]



SiCl_2 can easily be chemisorbed on C surface atoms and contribute to silicon formation unlike CH_4 as carbon source. The gas phase and the chemisorbed layer are enriched in effective silicon source species ($\text{SiCl}_3 + \text{SiCl}_2$) and depleted in effective carbon precursor (CH_3). These features favour a silicon excess in the deposits, which can act as a growth inhibitor leading to a nucleation regime and nanocrystals of $\text{SiC} + \text{Si}$.

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