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Investigation of the Chemical Vapor Deposition of Silicon Carbide from Tetramethylsilane by in Situ Temperature and Gas Composition Measurements

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The chemical vapor deposition (CVD) of silicon carbide (SiC) from tetramethylsilane Si(CH₃)₄ (TMS) on a graphite susceptor at 1200-1500 K is studied in a low pressure (≈100 Pa) cold-wall reactor under laminar flow conditions. In addition to material characterizations (electron microscopy and chemical analysis), the gas-phase temperature distribution and composition are investigated by combining several in situ and ex situ diagnostics. Coherent anti-Stokes Raman spectroscopy (CARS) on TMS and H₂ (produced from TMS decomposition) in the hot zone of the reactor gives the rotational temperature distribution of the molecules and their concentrations. Within a few mean free paths from the surface, the H₂ gas temperature is lower than the surface temperature. This is due to a nonunity accommodation coefficient α of H₂ on SiC. A simple analytical model yields $\alpha = 0.05$ for H₂ on SiC. Using gas transport coefficients and the experimental value of α for H₂, a two-dimensional numerical code is used to compute the gas flow and temperature profiles in the reactor. The increase of the H₂ concentration and the decrease of TMS concentration close to the surface reveals that gas-phase pyrolysis of TMS occurs within a few millimeters from the hot surface. The gas composition at the outlet of the reactor is analyzed by mass spectrometry and IR absorption spectroscopy. The global gas conversion and material balance between deposited SiC, powders, and exhaust gases is obtained. Si atoms of TMS molecules are mostly converted into solid SiC and powders. In the gaseous products a small fraction of trimethylsilane SiH(CH₃)₃ is detected. Other gases in decreasing order of importance are H_2 , CH₄, C_2H_4 , and C₂H₂. These results are compared with predictions of some thermodynamic models and chemical mechanisms reported in the literature.

I. Introduction

Among the products obtained by low pressure chemical vapor deposition (LPCVD), silicon carbide (SiC) is of great interest. In the aerospace industry, SiC finds very important applications because of its low density, its mechanical properties, and its chemical stability toward oxidation at high temperature. SiC can be deposited on various substrates or used in fiber production¹ to obtain composite materials. Its semiconducting properties are also under investigation.² The synthesis of SiC is often done by mixing two gases such as SiH4 and CH4, or from one gas containing both Si and C such as $Si(CH_3)_4$ (TMS) either by thermal CVD pyrolysis^{3,4} or plasma assisted CVD.⁵ In most cases, CVD processes are not well-known, and numerous experimental and theoretical studies are in progress.

These processes were first approached by ex situ diagnostic techniques, the different gaseous species being characterized before and after the chemical reaction and the solid deposit analyzed

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a posteriori. These methods do not allow a detailed comprehension of gas/surface phenomena. In order to identify the most important growth mechanisms, nonperturbative in situ diagnostics are needed. Temperature gradient and gas concentration measurements can be obtained by optical methods. Among these, laser induced fluorescence (LIF)^{6,7} and spontaneous Raman scattering⁸ are often used. Both of them are nonperturbative and allow spatially resolved measurements. LIF has the best sensitivity but is limited to the detection of species which have radiative excited states. Coherent anti-Stokes Raman scattering (CARS) has a better sensitivity than spontaneous scattering and is now used in several types of CVD reactors.9,10

In the present paper, we present spatially resolved temperature and concentration measurements obtained by CARS during the deposition of SiC from TMS pyrolysis in a LPCVD reactor. Other diagnostics are used to characterize the gas composition and the solid chemical and structural properties. The first part is devoted to the presentation of the experimental setup and of the different diagnostic techniques which have been used. In a second part, we present a thermal analysis of the different measurements and

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Figure 1. Schematic drawing of the LPCVD reactor.

a modeling of the reactor. The concentration measurements and a discussion about the involved chemical mechanism are presented in the last part of the paper.

II. Experimental Section

The experiment setup has been described elsewhere;¹¹ we just briefly list the salient features related to the present experiment.

II.1. LPCVD Reactor. The LPCVD reactor is a 55 cm high, $6 \times 7 \text{ cm}^2$ cross section water-cooled stainless steel duct (Figure 1) mounted vertically. The TMS gas passes through a mass flow controller and enters the bottom of the reactor with a typical velocity of 0.2 m s⁻¹. The gas is pumped out at the top by a primary pump. In such a way, the buoyancy force and the flow velocity vector are parallel. The pump limit vacuum is 2 Pa. TMS (Aldrich Chemie, 99.9% pure) is decomposed in front of a graphite 5890 (Carbone Lorraine) susceptor heated by the Joule effect (V = 6 V, I = 120 A). The susceptor is 5 cm long, 2.5 cm wide, and 2 mm thick. It has been designed in order to optimize the surface temperature uniformity and is inserted in one of the reactor walls so that the flow is not perturbed by geometric discontinuities. The surface temperature is measured either by a bichromatic pyrometer or by a 0.25-mm-diameter chromel-alumel thermocouple and is regulated by an Eurotherm controller. The reactor walls are maintained at 300 K by water cooling. The pressure which ranges typically between 100 and 1000 Pa is measured by a capacitive MKS Baratron gauge. This simple geometry has several advantages:

(a) A sharp temperature gradient is created, and the reaction zone is limited to a region close to the susceptor. Homogeneous deposition can be easily obtained because the mechanism is controlled by the surface reaction regime.

(b) The flow is of laminar type; it can be easily controlled and reproduced.

(c) For distances from the surface less than the susceptor width, modeling of the flow can be done using two-dimensional (2D) models.

The reactor is equipped with a 50-mm-diameter Pyrex window through which the pyrometer measures the surface temperature and two 35-mm-diameter dichroic windows for the laser and signal CARS beams.

II.2. In Situ CARS Diagnostic. In the following, the basis of the CARS technique is summarized (for details, see, for example, ref 12) and then particular attention is paid to data processing of TMS spectra.

II.2.1. Principle of CARS Measurements. A CARS signal is generated in a gaseous medium by the nonlinear optical interaction between a "pump" laser beam (at a frequency ω_P) with a "Stokes" laser beam (at a frequency ω_L). The signal frequency is $\omega_{AS} = 2\omega_P - \omega_L$. The coherent CARS signal is strong if $\omega_0 = \omega_P - \omega_L$ matches a Raman active vibration of the medium. These resonances are characteristic of one species, and the spectra can then be used to identify the different species which are present in a medium. Assuming no saturation effect occurs,¹³ the signal intensity I_{AS} is given in terms of the incident laser intensities and a third-order susceptibility $\chi^{(3)}$ which describes the optical properties of the gas:

$$I_{\rm AS} \propto I_{\rm P}^2 I_{\rm L} |\chi^{(3)}|^2 \tag{1}$$

where I_P and I_L are the intensities of the pump and Stokes laser beams. $\chi^{(3)}$ is given by

$$\chi^{(3)} = \frac{N}{h^3} \sigma \sum_{nn'} (\rho^{(0)}{}_{n'n'} - \rho^{(0)}{}_{nn}) \times \int_0^{\infty} \frac{g(v_z) \, dv_z}{\omega_P - \omega_L + \omega_{nn'}(1 - (v_z/c)) - i\Gamma_{nn'}} + \chi^{(3)}{}_{NR} (2)$$

where N is the number density in the sample volume, σ is the Raman cross section, and h is the Planck constant. The sum is over all the possible Raman active vibrations $\omega_{nn'}$ coupling each initial state n' (having $\rho^{(0)}_{nn'}$ population probability) with each final state n (having $\rho^{(0)}_{nn'}$ population probability). $\Gamma_{nn'}$ is the damping factor due to molecular collisions. The Doppler broadening is taken into account by the factor $\omega_{nn'}v_z/c$ where v_z is the projection of the velocity along the difference of wave factors $(K_P - K_L)$. $g(v_z)$ is the Maxwell-Boltzmann velocity distribution function. $\chi^{(3)}NR$ is the nonresonant susceptibility due to electron contribution and far-lying Raman resonances.

11.2.2. Data Processing. Expression 2 shows that the shape of the CARS spectrum depends on the temperature through the term $\rho^{(0)}_{n'n'} - \rho^{(0)}_{nn}$, while its amplitude depends on both the temperature and the density. For diatomics, expression 2 is easily calculated because the spectroscopic parameters and the Raman line widths are known. Then data processing is done by comparing the experimental spectra with the computed one and by using a calibration spectrum recorded for known pressure and temperature. We use here a simplified procedure developed for spectra composed of isolated Q lines.¹³ Its use is particularly suitable for interpreting the J = 0-5 Q lines of H₂,¹⁴ which are probed in the CVD reactor.

For polyatomic molecules such as TMS, interpretation of the spectrum is more complicated than for H_2 . A complete fit of the spectra yielding both temperature and TMS number density is not easily performed because of the lack of the required information. Despite that difficulty, TMS densities can be deduced from the peak amplitude of the CARS spectra because the temperature is already known (for instance from spectral shape analysis of H_2 CARS spectra). A very simple model has been developed to predict the temperature dependence of the CARS peak amplitude generated by 1 mol of TMS. The calculation is performed assuming coarse simplifications.

(1) In eq 2, only the Q lines ($\Delta v = 1$, $\Delta J = 0$) are considered.

(2) The TMS Raman line widths are supposed to be constant in the limited temperature and pressure ranges encountered in the reactor because collisinal and Doppler broadening are in the same order of magnitude and have opposite contributions.

(3) Among the 45 normal vibration modes of TMS, the ω_3 symmetric stretching of the SiC bond has been chosen because it is characteristic of TMS dissociation. It is easily broken as soon as an energy excess is given to the molecule. This stretching gives rise to an intense Raman transition of A₁ symmetry. Its maximum intensity is at 593 cm⁻¹ at 300 K. The population of the different energy levels contributing to the CARS signal is calculated by assuming TMS to be a tetrahedral molecule with one point of atomic weight 28 (Si) and four points of atomic weight 15 (CH₃). The calculation of moments of inertia gives a rotational constant B_0 of 0.102 cm^{-1,15}

The population probability $\rho_{nn}(v,J)$ of a (v,J) level is then given by

$$\rho_{nn}(v,J) \propto \frac{e^{-G_0(v)/k_{\rm B}T}(2J+1)^2 e^{-F(J)/k_{\rm B}T}}{Q_v Q_{\rm r}}$$
(3)

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Figure 2. Temperature behavior of the maximum amplitude of $\chi^{(3)}$ for 1 mol of TMS. Calculations are normalized to the amplitude obtained at 300 K: (full curve) theoretical results; (+) experimental results recorded at surface temperature for which no dissociation occurs.

where $G_0(v) = v\omega_3$ with $\omega_3 = 607 \text{ cm}^{-1.16}$ is the vibrational energy above the fundamental. $F(J) = B_v J(J+1)$ is the rotational term, B_v is the rotational constant for the v level. k_B is the Boltzmann constant. Q_v and Q_r are the vibrational and rotational partition functions, respectively. For a tetrahedral symmetry

$$Q_{\rm r} = \sum_{\rm r} (2J+1)^2 \exp(-B_0 J (J+1)/k_{\rm B} T)$$
(4)

(4) To calculate the vibrational partition function Q_{v_y} the effects due to the existence of other vibrational modes are not considered. In other words, the combination bands are assumed to overlap the fundamental band or to be unpopulated. Then

$$Q_{\rm v} = (1 - e^{-\omega_3/k_{\rm B}T})^{-1}$$
(5)

(5) Contributions of the hot vibrational bands are assumed to be partially superimposed to the fundamental band, and we have added the contribution of the first hot band with the fundamental one. The Raman cross sections of the hot bands is v + 1 larger than those of the fundamental band.

The J quantum number at the maximum amplitude J_{max} is obtained by deriving eq 3. Then, the peak amplitude is calculated using eqs 1-3 in which the J quantum number is replaced by J_{max} . The peak dependence versus the temperature is shown in Figure 2. Comparisons with experimental results recorded around 1000 K, using as a calibration the 300 K spectrum, are also shown. Validation of the model at higher temperature cannot be done because dissociation of TMS then occurs. Agreement between predictions and experiments below 1000 K is better than 10%. Cross comparisons of different results at temperature between 1000 and 1300 K indicate similar accuracy.

11.2.3. CARS Experimental Setup. The CARS spectral analysis is done by scanning CARS, i.e. by recording the intensity $I_{\rm AS}$ as a function of $\omega_{\rm P} - \omega_{\rm L}$. The $\omega_{\rm P}$ frequency is fixed and delivered by a frequency-doubled single mode Nd:YAG laser, while $\omega_{\rm L}$ is tunable and generated by a dye laser. The $\omega_{\rm P}$ and $\omega_{\rm L}$ laser energies are 50 and 2 mJ, respectively. The ω_L line width is 0.06 cm⁻¹. The ω_L frequency is scanned in steps of 0.015 cm⁻¹. The ω_P and ω_L laser beams have parallel polarizations. They are focused in a cell filled with 8×10^4 Pa of argon where a reference CARS signal is generated and then in the test cell where the sample CARS signal is created. The sample signal is then ratioed to the reference one in order to reduce the effects of laser fluctuations.¹³ The laser beams can be arranged in three different ways to achieve the required momentum conservation: collinear arrangement and planar or folded boxcars.¹² The choice between the three arrangements depends on spatial resolution criteria and also on the efficiency of optical filters used to separate signal and laser beams. Most of these experiments are made using the planar boxcars arrangement, the folded boxcars configuration being used only to record TMS spectra. In both cases, the probe volume in

TABLE I: Comparison between Thermal Measurements Using Different Methods

T _{CARS} (K)	T _{pyrometer} (K)	T _{thermocoupie} (K)
	1200	1175
	1255	1220
	1300	1275
1375 ± 16	1375	
1500 ± 11	1475	
1528 ± 17	1525	

the test cell is a 20-mm-length, $200-\mu$ m-diameter cylinder. The temperature and concentration profiles are measured by moving the reactor horizontally or vertically along the axis x or z, which are orthogonal to the axis of the cylindrical probe volume (Figure 1).

II.3. Ex Situ Analysis of the Gas Phase. The gas mixture at the exit of the CVD reactor is analyzed by both infrared absorption and mass spectrometry. For infrared analysis, the gas is sampled at the top of the reactor in a 1-m optical length multipass cell (Perkin-Elmer Model 580B) and then transported to the infrared spectrometer. For mass spectrometry analysis, a quadrupole Riber mass spectrometer is used. After the chemical reaction zone, a small part of the flow enters the mass spectrometer through a microleak valve. The pressure in the mass spectrometer is always kept under 10^{-4} Pa. The current intensity in the filament is 0.5 mA, and masses from 0 to 100 amu are detected. The spectrum is recorded with a three channels Visicorder Honeywell recorder. The acquisition time is 3 s/spectrum. The linearity of the apparatus versus the reactor pressure is checked until 7 × 10^{4} Pa.

The partial pressures of the gases in the mixture are obtained by fitting the experimental spectrum by a linear combination of pure gases spectra recorded in calibrated mixtures (Air Liquide). The relative intensities of the different peaks of each species are compared with those taken from mass spectral data.¹⁷

II.4. Ex Situ Analysis of the Solid. Several analysis methods are used for characterization of the SiC deposit. X-ray diffractometry is used to study the crystalline state with the Cu K α radiation. Scanning electron microscopy (SEM) is used to study the deposition morphology. The nature of the SiC bond on the surface is characterized by electron spectroscopy for chemical analysis (ESCA). The ratio Si/C is measured by chemical analysis and Castaing microprobe. The latter technique is also used to study the evolution of the deposit stoichiometry during the deposition process by analyzing a slice of the sample.

III. Thermal Analysis

III.1. Experimental Results. In a preliminary step, the bulk temperature and the surface temperature of the sample and the gas-phase temperature are compared. A graphite sample was specially designed. Thicker than the usual one, a 2-mm-diameter hole is drilled in it which allows the laser beams to go through the sample. This sample is then used as a small furnace installed in the reactor filled with 3000 Pa of H_2 . The gas temperature is measured by CARS while the external surface temperature is measured by the pyrometer and the bulk temperature is measured by a 0.25-mm-diameter chromel-alumel thermocouple inserted in the sample. Surface temperature and bulk temperature are expected to be very close because the temperature gradient in the sample is calculated to be less than 20 K knowing the heat conductivity of the graphite 5890 (k = 0.45 W cm⁻¹ K⁻¹ at 1500 K). The measurements are presented in Table I. They are always in agreement within $\pm 2\%$.

In order to separate pure thermal effects from the effects due to a chemical reaction, two thermal mappings are successively done. The thermal-transfer phenomena are first studied by flowing H_2 through the reactor, and then thermometry is done using H_2 formed by TMS pyrolysis.

(a) For pure H₂ flow, Figure 3 shows the temperature profiles along the axis x in front of the center of the hot sample (z = 0). The H₂ flow rate is 260 cm³ min⁻¹, the pressure is 133 Pa, and the surface temperature, T_S , is 1520 K. The hot surface is made of graphite or CVD deposited SiC. These profiles show that the



Figure 3. Rotational temperature profile of pure H_2 in front of a C surface (**■**) or a SiC surface (**●**). The surface temperature is 1520 K, and the H_2 pressure is 133 Pa. The full lines are calculated profiles (see section III.4).



Figure 4. H₂ rotational temperature at 0.5 mm from a C surface as a function of the pressure. $T_{\rm S} = 1520$ K. Temperature accuracy at one standard deviation ± 25 K. The solid line interpolates the experimental points.



Figure 5. Rotational temperature of H_2 produced by decomposition of TMS in front of a SiC surface. The surface temperature is 1520 K. The full line is a calculated profile (see section III.4).

gas temperature is lower than the surface temperature even at distances from the surface of the same order of magnitude than the mean free path. This temperature jump is a function of the nature of the surface. As shown in Figure 4, it is also a function of the pressure, decreasing when the pressure increases, but it is independent of the gas flow for flow rate up to 3 L min⁻¹.

(b) When H₂ is formed by TMS pyrolysis, the measurements are always obtained in front of susceptors covered with SiC. Although SiC deposit occurs during the experiment, the nature of the surface remains unchanged. The temperature profile obtained along the x axis for typical deposition conditions (TMS flow rate = 65 cm³ min⁻¹, $T_S = 1520$ K, P = 133 Pa) is presented in Figure 5. Note that the pressure of 133 Pa is measured when



Figure 6. Rotational temperature profile along the z axis (x = 0.5 mm) of H₂ produced by decomposition of TMS in front of a SiC surface. The surface temperature is 1520 K. The solid line interpolates the experimental points.



Figure 7. Rotational temperature of H₂ produced by TMS pyrolysis in front of the center of the sample (x = 0.5 mm, z = 0) as a function of surface temperature. The solid line interpolates the experimental points.

 $T_{\rm S} = 300$ K. The pressure increases to 160 Pa when the sample is heated to 1520 K. Figure 5 shows that the temperature jump is still present, but weaker: around 100 K instead of 545 K for pure H₂ on SiC without CVD (Figure 3). As for the pure H₂ flow, it is independent of the flow rate. The temperature profile along the z axis is presented in Figure 6 at x = 0.5 mm from the surface. The presence of H₂ upstream (z < -15 mm) reflects the large diffusivity of H₂. In front of the sample (-15 < z < +15 mm), the temperature is rather constant. Figure 7 gives the H₂ rotational temperature as a function of the surface temperature at 0.5 mm from the sample (order of magnitude of one mean free path). Between 1300 and 1500 K, the gas temperature increases with the surface temperature. Above 1500 K, the gas temperature stays almost constant.

III.2. Modeling of the Gas Flow and Temperature Profiles in the Reactor. Modeling of temperature profile is done using a Fortran code named MOCROI.¹⁸ The differential equations implied by mass conservation, momentum conservation, and energy conservation are locally resolved. The physical quantities which are calculated at every calculation step are momentum, density, and enthalpy. They are directly related to the velocity and temperature.

At the entrance of the reactor, the flow rate and enthalpy are fixed. The static pressure is fixed at the exit. The density is then calculated from the state equation. At the cold wall, the temperature is fixed at 300 K. The mean molar weight, the viscosity μ , the thermal conductivity k, the Prandtl number Pr, and the heat capacity C_P are used to characterize the gas and must be fixed in the code. The MOCROI code was initially devoted to the calculation of continuous flow. The observed temperature jumps show that such a description is not accurate for this reactor, at least locally. This is confirmed by evaluating the Knudsen number Kn, the ratio between the mean free path (λ) and a characteristic

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TABLE II: Accommodation Coefficients Calculated for H_2/W , H_2/C , and H_2/SiC Systems

	$(\partial T/\partial x) _{wall}$		
gas/solid system	(K cm ⁻¹)	ΔT (K)	α
H ₂ /W	18 800	355	0.10
H ₂ /C	29 100	310	0.1
H ₂ /SiC	19 200	545	0.0
H ₂ produced by TMS pyrolysis/SiC	29 700	100	0.0

dimension of the flow (L). λ is easily calculated (10⁻⁴ m for our flow conditions), but L is rather ambiguous. Choosing for L the distance on which the flow macroscopic parameters have significant evolution (L < 1 cm), one obtains Kn > 0.05 which is near the usual limit for continuous flow (Kn < 0.1).¹⁹ A solution consists of keeping the continuous description but replacing the usual boundary condition $T_{gas} = T_S$ by $T_{gas} = T_S - \Delta T$ where the temperature jump ΔT is written^{19,20}

$$\Delta T = \frac{2 - \alpha}{\alpha} \frac{2\gamma}{\gamma + 1} \frac{\lambda}{Pr} \frac{\partial T}{\partial x}$$
(6)

where $\gamma = C_P/C_V$ = ratio of the heat capacities (≈ 1.4), α = accommodation coefficient, and $\partial T/\partial x$ = gas temperature gradient along the axis perpendicular to the wall.

For slip flow, a slip condition together with a temperature jump should be introduced. However it is not required here because, the maximum velocity being low ($\approx 1 \text{ m s}^{-1}$), the temperature profile is independent from the boundary flow velocity. So only a temperature jump is introduced. At time t = 0, the fluid is static at 300 K. Experimental conditions are progressively applied during the first steps of calculation by raising the substrate temperature.

This 2D code is applied to the CVD reactor by making the dimension y infinite (this approximation limits the validity of the computation to the region close to the surface since the width of the sample is only 2.5 cm). A grid with rectangular mesh and variable steps is used to model the reactor geometry. The net is denser in front of the sample where the strong gradients are located. Figures 3 and 5 show that the agreement between calculation and experimental measurements is quite good. An example of a velocity map calculated with this code is presented in Figure 8.

(a) In the case of pure H₂, the best fits between experimental and theoretical profiles (Figure 3) yield to the values of $\alpha = 0.05$ for H₂/SiC and $\alpha = 0.15$ for H₂/C. The accommodation coefficient measured for H₂/W ($\alpha = 0.10$) is reported in ref 21; it is discussed in terms of a chemisorption mechanism. The data are summarized in Table II.

(b) For the case of H₂ produced by dissociation of TMS, the shape of the temperature profile (Figure 5) remains comparable with those shown in Figure 3, indicating that it is mainly due to the heat transfer in the gas. Using the MOCROI code in which no chemical reaction are involved, the profile is fitted by a calculation done for a mixture of 50% H₂ and 50% TMS. An accommodation coefficient $\alpha = 0.05$ is deduced. It is equal to the value previously found for pure H₂ on SiC. However, the agreement may be fortuitous because the surface coverage can be affected by the presence of TMS or radicals formed during the TMS pyrolysis which in turn may change the energy exchanges at the surface.

IV. Chemistry

All the results presented in this part are obtained with the same experimental conditions: the surface temperature is 1520 K, the TMS pressure is 132 Pa, and the TMS flow rate is $65 \text{ cm}^3 \text{ min}^{-1}$.

IV.1. Mass Transfer and Gas Conversion. *IV.1.1.* Solid Analysis. SiC Deposit. The SiC is deposited on graphite with a deposition rate of 400 μ m/h. It is shown to be crystallized in the β -phase by X-ray diffraction. The deposit has a rather homogeneous appearance. After Ar⁺ beam cleaning, Si, C, and a small amount of O are identified on the surface (ESCA). The microprobe C K α signal obtained on a polished slice of this sample is identical to the signal of a sintered reference SiC sample (position and bandwidth). These physical techniques are com-





Figure 8. 2D simulation of the velocity distribution in the reactor with a 100 K temperature jump at the hot surface at 1520 K and a flow velocity of 0.2 m s⁻¹ at the entrance of the reactor.

pleted by chemical analysis of the deposit. The ratio Si/C is equal to 1. Figure 9 shows a scanning electron microscopy (SEM) picture of the interface between the substrate and the SiC deposit after chemical etching in a Murakami mixture (10 cm³ NaOH, 10 cm³ Fe(CN₆)K₃, 100 cm³ H₂O). The chemical treatment reveals columnar features of various sizes: ~ 1 , ~ 10 , and $> \sim 50$ μ m due to a conic type of growth from initial nucleation on the substrate. As the cones develop and intersect, larger columnar features appear. This phenomenon is generally observed for various CVD processes and has been analyzed in terms of fractal geometry.²²

Powders. Some powders are found in the reactor or on its walls. They are analyzed by infrared absorption (Figure 10). Yellowwhite powders are found in the cold regions. The SiC, SiH, SiCH₃, and SiO vibrations are identified. These powders are probably initiated by gas-phase nucleation from radical molecule reactions as the gas cools down. In the dark powders found into the hot

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Figure 9. SEM photograph of SiC deposited on graphite at the 1520 K surface temperature. The interface between substrate and SiC is at the top of the picture.

TABLE III: Partial Pressures of the Different Species at the Exit of the Reactor after Thermal Decomposition^a

partial pressure (Pa)			partial pressure (Pa)		
TMS	86	C ₂ H ₂	9		
CH₄	11	H_2	43, 47*		
C_2H_4	10	(CH ₃) ₃ SiH	2.7**		

^aMeasurements are made by mass spectrometry, CARS (indicated by a single asterisk), and IR absorption (indicated by double asterisks).

zone of the reactor, only SiC is identified. This second type of powders probably originate from peeling of some parts of the deposit and/or gas-phase nucleation close to the hot surface.

IV.1.2. Ex Situ Gas-Phase Analysis. By comparison with the vibrational spectra of pure species and literature data, the different peaks of the infrared spectrum of the gas sampled at the exit of the reactor are assigned (Figure 11). The most abundant species is TMS and the less abundant $(CH_3)_3SiH$.

The partial pressures are summarized in Table III. For these species, except $(CH_3)_3SiH$, partial pressure measurements are made by mass spectrometry while the hydrogen partial pressure is also measured by CARS. The mass spectrometry spectra are processed according to the method discussed in section II.3. The contribution of the different species to the spectrum of the gas mixture is shown in Table IV. The accuracy of the measurement is 1.5 Pa for TMS, and the relative precision for other species is typically 5–10%. H₂ partial pressures measured by CARS are consistent with those derived from mass spectrometry, which supports the validity of the method.

Comments. From the infrared spectrum, the $(CH_3)_3SiH$ pressure is estimated to be around 3 Pa. However, this molecule is not detected by mass spectrometry, although its main peak at m/e = 59 corresponding to the fragment $(CH_3)_2SiH$ is apart from any peak of TMS.¹⁷ The sum of the partial pressures (Table III) is 3 Pa less than the total pressure measured by the Baratron gauge, which is consistent with the uncertainty domain. The gas-phase composition is quite different from the composition



Figure 10. Infrared spectrum of the powders found in the LPCVD reactor after a deposition experiment: (a) yellow-white powders found on the cold walls; (b) dark powders found in the hot zone of the reactor.





Figure 11. Infrared spectrum of the gas at the exit of the reactor after thermal decomposition. The absorption lines are labeled using literature classification: TMS, ref 15; $(CH_3)_3SiH$, ref 41; CH_4 , C_2H_2 , and C_2H_4 , ref 42.

observed in several other studies.²³⁻²⁷ In particular, we observe no C_2H_6 , and the H_2 partial pressure is quite large. These observations will be discussed later.

IV.1.3. Material Balance. From the SiC growth rate and from partial pressure measurements, it is deduced that 35% of TMS is decomposed in the reactor and 20% of the injected TMS is converted into SiC. Except TMS, there is almost no species containing Si in the gas phase at the reactor exit except the small fraction of $(CH_3)_3SiH$. The material balance can then be written

$$100Si(CH_{3})_{4} \rightarrow 65Si(CH_{3})_{4} + 35H_{2} + 7C_{2}H_{2} + 7C_{2}H_{4} + 8CH_{4} + 3(CH_{3})_{3}SiH + 20SiC + 12SiC_{x}H_{y}$$
 (7)

The coefficients for the different species are measured with an accuracy of ± 1 . The balance for C and H would result in a value of $x = 6 \pm 1.5$ and $y = 20 \pm 2$ for the SiC_xH_y compound. This SiC_xH_y compound corresponds probably to the yellow-white powders which are found in the reactor. It contains SiH and SiCH₃ groups (see Figure 10), but it is mostly composed of a polymeric carbon network. As stated above, these powders probably originate from radicals which could not react on the surface and which are then carried away in the cold zone. This observation indicates that the decomposition of TMS is faster than the deposition reaction.

IV.2. In Situ Partial Pressure Measurements. In this part, we present the in situ gas-phase concentration measurements obtained by CARS. CARS was used in an attempt to detect the different species identified by ex situ measurements or some intermediate radicals.

TABLE IV: Mass Spectrum Intensities and Attribution of the Gas at the Exit of the Reactor after Thermal Decomposition

	<i>m/e</i> 2	m/e 73	m/e 45	m/e 26	m/e 15	<i>m/e</i> 16	m/e 43	m/e 28	m/e 27	m/e 25	m/e 88	m/e 24	
gas mixture	543	485	150	131	112	111	100	95	60	30	10	6	
TMS	49	485ª	147		34	17	97	5			11		
CH ₄	4				75	94ª							
C_2H_4	4			56				90ª	58	11			
C_2H_2	3			75ª						17		6	
H.	483												

^a Points out the main peak of each species.



Figure 12. H₂ partial pressure in front of the center of the sample (z = 0) as a function of x. Surface temperature is 1520 K and flow rate is 65 cm³ min⁻¹.



Figure 13. H_2 pressure profile along the z axis (x = 0.5 mm). H_2 is produced by decomposition of TMS in front of a SiC surface. The surface temperature is 1520 K.

IV.2.1. H_2 Partial Pressure. Figures 12 and 13 present the x and z profiles of the H_2 pressure for typical deposition conditions (TMS flow rate = 65 cm³ min⁻¹, $T_S = 1520$ K, P = 133 Pa). They show that H_2 is by far the most abundant species produced by dissociation of TMS and also that the pressure gradient is sharper along z (near the borders of the sample) than along x. This last point is explained by the steep temperature gradient in the z direction which results in a strongly varying H_2 production rate from gas-phase reactions. Also, the diffusion occurs faster in the x direction than in the z direction where the gradient is very steep. Figure 12 shows also a gentle increase of the H_2 partial pressure very close to the surface, which seems to indicate that at least part of H_2 is produced on the surface.

IV.2.2. TMS Partial Pressure. Results are presented in Figure 14. The TMS pressure is almost constant (≈ 60 Pa) between 5 and 20 mm from the surface and decreases down to 33 Pa at 0.5 mm from the surface. This decrease in the TMS pressure indicates that the decomposition of TMS is localized within a few millimeters from the surface, as it will be shown in the Discussion (section IV.4).

IV.2.3. Methane, Ethylene, and Acetylene. In the reaction zone (at 0.5 mm from the surface), the pressure of H_2 and TMS is 115 Pa. The total pressure is 165 Pa. Then the sum of partial pressures for other species is around 50 Pa. As CH₄, C₂H₄, and C₂H₂ are present at the exit of the reactor, CARS was used to look for them in the reaction zone. The characteristic frequencies of these molecules are well-known, but no signal was detected in deposition conditions. An attempt to record spectra of pure samples of each gas has shown that these products cannot be detected at partial pressure below 100 Pa. Then the lack of sensitivity does not allow us to know if they are present in the reaction zone at densities below the lowest detection. Then, other



Figure 14. TMS pressure profile as a function of the distance from the surface during the deposition experiment.

TABLE V:	Thermodynamic Previsions of the Pa	artial Pressures of
Gaseous Sp	ecies from Refs 29 and 30	

	$CH_4 + SiH_4$ [P = 100 Pa, ref 30]	$Si(CH_3)_4$ [P = 133 Pa, ref 29]				
	T = 1000 K	T = 1000 K	T = 1200 K	T = 1400 K		
$H H_2$ SiH ₄ CH ₄ CH ₃ SiH Si C ₂ H ₂ C ₂ H ₂	$\begin{array}{c} 0.71 \times 10^{-5} \\ 0.10 \times 10^{3} \\ 0.63 \times 10^{-7} \\ 0.38 \times 10^{-5} \\ 0.55 \times 10^{-11} \\ 0.39 \times 10^{-10} \\ 0.16 \times 10^{-10} \end{array}$	$\begin{array}{c} 0.75 \times 10^{-5} \\ 0.13 \times 10^{3} \\ 0.20 \times 10^{-1} \end{array}$	$\begin{array}{c} 0.65 \times 10^{-3} \\ 0.13 \times 10^{3} \\ 0.43 \times 10^{-2} \\ 0.37 \times 10^{-6} \\ \end{array}$ $\begin{array}{c} 0.16 \times 10^{-4} \\ 0.26 \times 10^{-6} \end{array}$	$\begin{array}{c} 0.16 \times 10^{-1} \\ 0.13 \times 10^{3} \\ 0.87 \times 10^{-3} \\ 0.26 \times 10^{-5} \\ 0.33 \times 10^{-6} \\ 0.39 \times 10^{-3} \\ 0.45 \times 10^{-6} \end{array}$		

species present in the reaction zone should essentially be radical species. The validity of these assumptions can be checked by thermodynamic calculations.

IV.3. Comparisons with Thermodynamic Calculations. Some thermodynamic equilibrium calculations (see for example ref 28 for the principle of such calculations) predict a codeposition of SiC and C from TMS.²⁹ The experimental results show that it is possible to achieve SiC deposition with very little excess C. This observation shows that these calculated results must be taken with care. About the gas phase, the main results from refs 29 and 30 are presented in Table V. Although the species considered at the beginning of the reaction are different, $SiH_4 + CH_4^{30}$ or TMS,²⁵ the results of Aubreton²⁹ and Kingon et al.³⁰ indicate the same order of magnitude for the partial pressures of the different gaseous products at 1000 K. As the intermediate and final products considered in the calculation are almost identical, this fact is not a surprise. The gas phase is composed essentially of H_2 , which is 10⁴ times more abundant than the next species. For a temperature above 1200 K, the next product in abundance is H radical, which we are not able to detect. Small concentrations (below 10^{-5} Pa) of CH₄, C₂H₄, and C₂H₂ are also predicted.

It is evident that in this study, the gas phase does not achieve thermodynamic equilibrium due to the short residence time in the reaction zone and to the surface limited process. The steep temperature gradients in the reaction zone create gradients in the thermochemistry of the system. Therefore it is not surprising that the gas-phase composition measured at the exhaust of the reactor differs considerably from steady-state homogeneous thermodynamic predictions at high temperature. However the computations of ref 29 at different temperatures indicate the general trends in the gas-phase evolution (decrease of CH_4 versus C_2H_2) and the major radical species (H and CH_3) which can be expected when the hottest part of the reaction zone is approached or when the nominal surface temperature of the susceptor is increased. This thermodynamic approach must be complemented by a kinetic approach based on a reaction scheme, as discussed below.

IV.4. Discussion. *IV.4.1. Homogeneous Gas-Phase Pyrolysis of TMS.* TMS pyrolysis was studied for the first time in 1937,³¹ but the decomposition mechanism is still very uncertain. For the



Figure 15. Computed variation of the first-order rate constant k_1 for TMS dissociation as a function of the distance from the surface assuming a temperature gradient derived from measurements shown in Figure 5.

homogeneous TMS decomposition process, the initial step generally admitted is the first-order reaction

$$Si(CH_3)_4 \rightarrow Si(CH_3)_3 + CH_3 \tag{8}$$

with a kinetic constant k_1 (s⁻¹) given by the formula $k_1 = A \exp(-E_A/RT)$, where A is the Arrhenius factor and E_A is the activation energy (kJ/mol⁻¹). At temperatures above 950 K, Baldwin et al.²⁵ determined $k_1 = 10^{17.6} \exp(-355/RT)$. Assuming that the gas temperature profile along the x axis is identical to the measured H₂ rotational temperature profile given in Figure 5, the spatial variation of k_1 is computed (Figure 15). The decay of k_1 is very fast for 0 < x < 4 mm, i.e. on the distance where the measured TMS partial pressure decreases (Figure 14). In this region the balance equation for TMS can be written:

$$-\frac{\partial}{\partial x}\left(D \;\frac{\partial N}{\partial x}\right) = S(x) - N(x) \;k_1(x) \tag{9}$$

where N(x) is the TMS density (which can be derived from the P(x) and T(x) profiles of Figures 14 and 5, respectively), D the diffusivity (slowly varying with gas temperature and gas composition), and S(x) the source term of TMS. Because $\partial N/\partial x$ is a positive but decreasing function of x, the right hand side term of eq 9 should be positive which means that $S(x) > N(x) k_1(x)$. S(x) is rather complicated to estimate since it includes both the transport of TMS due to the laminar gas flow parallel to the zaxis and also diffusion in the y-z plane from the cold wall regions toward the heated substrate (diffusion along the y axis is probably as important as diffusion along the z axis since the substrate width is only 2.5 cm as compared to 7 cm for the width of the duct). Actually the laminar gas flow velocity along the z axis yields an average residence time for the TMS of about 0.1 s along the 5-cm length of the substrate (see Figure 8) while the typical time of decomposition $1/k_1$ is about 10^{-4} s in front of the substrate. Presence of TMS close to the surface indicates that the dominant source term of TMS at the hot surface should be lateral diffusion.

Although eq 9 cannot be readily solved, except by a numerical model (presently under development from the MOCROI code), the total amount of decomposed molecules can be estimated by integrating $N(x) k_1(x)$ along the x axis and multiplying the result by the area of the substrate which is homogeneously heated, i.e. about 6–10 cm². One obtains a number of $\approx 5 \times 10^{19}$ decomposed TMS molecules/s which exceeds the flow rate of TMS molecules: 3×10^{19} /s corresponding to 65 cm³ min⁻¹, whereas the material balance equation (eq 7) shows that only 35% of the TMS is decomposed. A better agreement would be obtained by slightly decreasing the value of the A preexponential factor and slightly increasing the activation energy E_A in the expression of k_1 within the experimental uncertainties given in ref 25. Using $A = 10^{17.3}$ and $E_A = 361 \text{ kJ/mol}$, the computed number of decomposed molecules becomes 1.4×10^{19} /s which is compatible with experimental results. Such an agreement is very satisfactory in view of the assumption made on the temperature profile of the gas. The gas temperature has been taken as identical to the measured

H₂ rotational temperature, with a difference of ≈ 100 K at x = 0 with respect to the surface temperature $T_S = 1520$ K. This difference has been attributed to the low accommodation probability of H₂ on SiC, but we do not know the accommodation probability of TMS on SiC. Nevertheless after a few mean free paths from the surface, rotational and translational temperatures of all molecules should be equilibrated. If we had taken a temperature profile starting from $T(x=0) = T_S$, the computed decomposition rate of TMS would have been 10 times larger and in severe contradiction with experimental results.

IV.4.2. Secondary Gas-Phase Reactions. After the initial dissociation of TMS into methyl (CH₃) and trimethylsilyl [Si-(CH₃)₃] radicals, several different prolongation and recombination processes have been proposed to explain polyorganosilane products or SiC deposition.²³⁻²⁷ Most of the proposed reaction schemes predict essentially CH₄, C₂H₆, C₂H₄, and C₂H₂ production, while we find that H₂ is the most abundant product and that C₂H₆ is not detected. Our results are quite difficult to compare to previous ones obtained at higher pressures and lower temperatures, which could lead to more complex chemical species. Also the transit time in the reaction zone is rather short, and the gas-phase evolution is stopped by evacuation in the cold zone. Taylor and Milazzo²⁷ have studied the ratio between C₂H₄ and C₂H₆. They show that this ratio increases with temperature from 1000 to 1150 K. This result, extrapolated to 1520 K, would lead to a very low C₂H₆ pressure, consistent with our observations.

A possible scheme for the gas-phase evolution could be based on unimolecular reactions with few intermediate steps as proposed by Baldwin et al.²⁵ and Taylor and Milazzo.²⁷ According to the simple scheme of Taylor and Milazzo Si(CH₃)₃, Si(CH₃)₂, and Si(CH₃) radicals can dissociate in rapid succession, releasing one CH₃ radical at each step. Actually for trimethylsilyl dissociation

$$Si(CH_3)_3 \rightarrow Si(CH_3)_2 + CH_3 \tag{10}$$

the activation energy of 220 kJ/mol^{25} is smaller than the 355 kJ/mol for TMS dissociation. In comparison spontaneous dissociation of methyl radicals

$$CH_3 \rightarrow CH_2 + H$$
 (11)

$$CH_1 \rightarrow CH + H_2$$
 (12)

is very unlikely in view of the large dissociation energies of 460 and 450 kJ/mol, respectively.³²

Secondary reactions of CH_3 or $Si(CH_3)_{n\leq 3}$ radicals with TMS can produce CH_4 and trimethylsilane $(CH_3)_3SiH$ and new radicals such as $(CH_3)_3SiCH_2^{25}$

$$CH_3 + Si(CH_3)_4 \rightarrow (CH_3)_3SiCH_2 + CH_4$$
(13)

$$Si(CH_3)_3 + Si(CH_3)_4 \rightarrow (CH_3)_3SiCH_2 + (CH_3)_3SiH \qquad (14)$$

Subsequent dissociation of $(CH_3)_3SiH$ and $(CH_3)_3SiCH_2$ will produce the long-lived species $(CH_3)_2Si=CH_2$

$$(CH_3)_3SiH \rightarrow (CH_3)_2Si=CH_2 + H_2$$
(15)

$$(CH_3)_3SiCH_2 \rightarrow (CH_3)_2Si=CH_2 + H$$
(16)

 $(CH_3)_2Si \longrightarrow CH_2$ can be also produced by radical-radical reactions such as

С

$$H_3 + Si(CH_3) \rightarrow (CH_3)_2Si = CH_2 + CH_4$$
(17)

$$2\mathrm{Si}(\mathrm{CH}_3)_3 \rightarrow (\mathrm{CH}_3)_2\mathrm{Si=CH}_2 + (\mathrm{CH}_3)_3\mathrm{SiH} \qquad (18)$$

Recombination reactions between CH₃ and Si containing radicals also produce C_2H_6 and methylated disilane, but these species will decompose at high temperature. Taylor and Milazzo proposed a sequence of reactions initiated by CH₃ biradical recombination followed by CH₃ insertion into C_2H_6 and subsequent decomposition of reaction products into C_2H_4 and atomic H

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$$
(19)

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$
 (20)

$$C_2H_3 \rightarrow C_2H_4 + H$$
 (21)

Chemical Vapor Deposition of SiC from Si(CH₃)₄

Eventually, C_2H_2 is produced by H_2 elimination from C_2H_4 . Radicals will eventually diffuse to the hot surface or in the cold zone. Surface reactions of Si containing species are probably controlled by the coverage of CH₃. Surface reactions analogous to gas-phase reactions 13 and 17 lead to CH₄ elimination and creation of chemisorption sites for species such as (CH₃)₃Si, (CH₃)₃SiCH₂, or (CH₃)₂Si=CH₂ species. Further CH₄ and H₂ elimination proceeds by cross linking in the first few monolayers. A global activation energy of the process of 170 kJ mol⁻¹ can be derived from the temperature dependence of the deposition rate. SiC deposition from methyltrichlorosilane has been recently presented.^{33,34} From a thermodynamic study the authors propose a reaction scheme also based on CH₃ adsorption.

Powder formation in the cold regions of the reactor is probably due to chain polymerization of long-lived species such as $(CH_3)_2Si=CH_2.$

IV.4.3. Surface Pyrolysis and Surface Reactions. Although it has been shown that homogeneous gas-phase pyrolysis is consistent with experimental results, a second approach can be proposed: TMS is assumed to be pyrolyzed only on the hot substrate. Within this assumption, the density gradient $\partial N/\partial x$ can be related to the surface boundary condition with a loss probability β at the surface35

$$-D \frac{\partial N}{\partial x} = \frac{\beta}{(1 - (\beta/2))} N(x=0) \frac{v}{4}$$
(22)

where D is the diffusivity and v the mean thermal velocity. To compute the diffusivity of TMS in the gas mixture at 163 Pa within 4 mm from the surface, we consider the partial pressures of H₂ (80 Pa) and TMS (between 30 and 53 Pa) and the rest is assumed to be CH₄. The binary diffusivities for TMS in each gas at a temperature of 1400 K are computed for a Lennard-Jones (6-12) potential.³⁶ The Lennard-Jones parameters for H₂ are given in ref 36, and for CH₄ and TMS we used recommended values given in ref 37. Finally the diffusivity in the mixture is simply obtained from the Blanc formula, as in ref 35: $D \approx 0.06$ $\pm 0.01 \text{ m}^2/\text{s}$. From eq 22 and the experimental values of $\partial N/\partial x$ and N(x=0), we derive $\beta \approx 0.08 \oplus 0.02$. Within this hypothesis of surface pyrolysis, the net flux of TMS lost on the surface can be compared to the measured deposition rate (400 μ m/h) assuming a mass density for solid SiC of about 3 g/cm^3 . The equivalent deposition rate would be 4 times larger than the measured one. It can be assumed that only a fraction of the decomposed TMS molecules leads to SiC deposition, and the remaining fraction goes back to the gas phase as Si containing molecules or radicals distinct from TMS. Indeed the presence of trimethylsilane and Si containing powders in material balance of TMS (eq 7) reveals that partial recombination of TMS decomposition products occurs. However this represents less than 3/4ths of the decomposed fraction of TMS. Nevertheless the consistency within a factor of 2-3 with experimental results shows that both the homogeneous pyrolysis approach and the surface pyrolysis approach can be used with some internal consistency. As a matter of fact homogeneous pyrolysis occurs so close to the surface due to the sharp temperature gradient that it can be viewed as a surface controlled reaction.

V. Conclusion

Chemical vapor deposition of silicon carbide from pyrolysis TMS has been studied in a cold wall laminar flow reactor on a substrate heated at ≈ 1500 K.

CARS was used both for in situ temperature measurements, using the rotational spectrum of H₂, and for in situ measurements of H_2 and TMS partial pressures. H_2 rotational temperature measurements in front of the hot surface revealed a temperature jump between the surface and the gas. This has been interpreted in terms of temperature accommodation. From a simulation of the temperature profile using a numerical code for gas flow and temperature distribution in the reactor, the measured temperature jump was explained with an accommodation coefficient $\alpha \approx 0.05$ for H₂ on SiC at 1500 K.

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To our knowledge, it is the first time that CARS has been used for concentration measurements of TMS at high temperature, with the difficulty of disentangling the effects of temperature gradients and gas density variations on the evolution of the CARS spectrum. The decrease of TMS partial pressure close to the surface indicates that TMS pyrolysis is confined within a few millimeters due to the fast decay of the first-order rate constant for TMS dissociation along the temperature gradient.

The material balance was determined by ex situ measurements of the exhaust gas partial pressures and solid deposit analysis. For a 35‰ TMS conversion, the silicon containing products consist of 57% stoichiometric SiC deposit, 34% SiC_xH_v powders generated by polymerization in the cooling gas flow, and 9% of trimethylsilane (CH₃)₃SiH. The hydrocarbon gas products are CH₄, C₂H₄, and C_2H_2 , in approximately equal amounts, whereas no C_2H_6 is detected, in qualitative agreement with thermodynamic calculations. From these results some suggestions can be made about the gas-phase and surface mechanisms of TMS pyrolysis.

Some modeling studies of silicon carbide CVD starting from other gas precursors have been published.^{38,40} In particular, Stinespring and Wormhoudt³⁸ have developed a kinetic and thermodynamic numerical model for the CVD of SiC in a cold wall tubular reactor under laminar flow conditions which makes their experimental situation very similar to ours, although their gas precursor is a mixture of SiH_4 and C_3H_8 instead of TMS. However their analysis differs from ours by the fact that these authors have not considered the problem of temperature accommodation at the hot surface, which must be taken into account at low pressure.

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Electronic Structure of Nitrogen Square Planar Copper Complexes in Langmuir-Blodgett **Films**

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The Cu 2p and N 1s X-ray photoelectron spectra of nitrogen square planar copper(II) complex, derived from copper phthalocyanine and especially substituted to produce Langmuir-Blodgett (LB) films, are reported and compared with those of commercial copper phthalocyanine (CuPc) and selected porphyrin compounds. Although the copper atom is found primarily in the Cu(II) state, we observe the presence of the reduced Cu(I) form, with a great variety of relative intensities, because of a concomitant ability to reduction. In contrast, in the LB films, the copper atom remains in the Cu(II) state. We discuss this different behavior in terms of the reduction degree of the molecule, the localization of the additional electrons on the metal or the macrocycle, and a different nitrogen geometry around copper.

I. Introduction

The electronic structure of copper(II) compounds in a square planar environment is a matter of active interest because (i) the discovery of high- T_c superconducting materials has stimulated a number of studies¹ on the electronic properties of copper perovskites, in which the copper atom is found with four oxygen atoms in a square planar arrangement, and (ii) the search for conducting organic two dimensional thin films has favored the choice of substituted phthalocyanine compounds,² in which the copper atom is found in the middle of a nitrogen square plane.

The electronic and magnetic properties of these systems have been successfully probed by X-ray photoelectron spectroscopy (XPS). Copper oxides, for example, are considered as model systems for semiconductors. CuO is well established $^{3-5}$ to be a charge-transfer antiferromagnetic semiconductor with a small gap (1.4 eV), in which copper is in the Cu(II) state with an open shell 3d band. In contrast, Cu₂O is a textbook semiconductor (gap of 2.17 eV), in which the copper atom is in the Cu(I) state, i.e. in a situation closer to Cu metal,³ i.e. with a full 3d band. The Cu 2p spectrum³ of CuO shows two doublets separated by about 20 eV due to the spin-orbit splitting. Each doublet consists of one intense "main peak" $(E(2p_{3/2}) = 933.2 \text{ eV})$ and a broad satellite structure at some 9 eV toward high binding energy. According

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to previous experimental and theoretical studies,³⁻⁵ the formation of a 2p hole favors a charge transfer from the oxygen ligands onto the open 3d shell of the metal (main line) and strong 2p,3d electron interaction effects (satellite). In contrast, in Cu₂O, the 3d copper band is full, and there is no possible coupling of the 3d electrons with the 2p hole and the XPS spectrum is reduced to a single line $(E(2p_{3/2}) = 932.4 \text{ eV})$ with a very weak satellite. Very similar observations have been made on XPS spectra of high- T_c supraconducting materials.⁶ Other XPS studies of copper(II) compounds with ligands other than oxygen,⁷ including amorphous copper phthalocyanine,⁸ show that the satellite shape and its energy separation from the main peak depends significantly on the local symmetry and the nature of the ligand.

In this paper, we are considering a copper atom surrounded by four nitrogen atoms in a plane square geometry at the center of phthalocyanine and porphyrins systems (Figure 1). Among them, the so-called CuS18 one is of particular interest because its amphiphilic character favors the formation of Langmuir-Blodgett (LB) films.⁹ The CuS18 molecule is basically a copper phthalocyanine with four pyridine rings in the outskirts of the macrocycle, each pyridinic nitrogen atom being quaternized to attach a carbon chain. The main difference of such LB films with the same compound in the amorphous phase is that the molecule, when processed in LB films, is built-in in a reduced form $(CuS18_{LB}^{2-})$.⁹ In any of the complexes of Figure 1, the central

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