In-situ FTIR analysis of TEOS and HMDS low frequency plasmas

P. RAYNAUD, Y. SEGUI, M. LATRECHE, and R. DELSOL.
Laboratoire de Génie Electrique -URA 304 CNRS
UNIVERSITE PAUL SABATIER
118. route de Narbonne 31062, Toulouse - France

ABSTRACT

Hexamethydisiloxane and tetraethoxysilane monomers dissociation in a low frequency plasma have been studied. In situ FTIR analysis of the gaseous and plasma phases have been achieved in the mid IR range. The effects of gas pressure and low frequency power level have been investigated. TEOS appears to be more easily dissociable than HMDS. Saturation effect of the IR absorption have been recorded for HMDS plasma.

INTRODUCTION

Organosilicon plasmas have been used for a long time as deposition techniques of SiO_2 [low frequency (LF), radio frequency (RF), and microwave plasmas]/1,2/. The SiO group, which is the most interesting specie for this deposition process, is present in the structure of the Hexamethyldisiloxane (HMDS) and Tetraethoxysilane (TEOS) monomers. Different species, such as SiO, C_xH_y are created by the dissociation of the monomer molecules in the plasma reactor. It is difficult to know if the SiO species are the main species which react with the surface to be deposited or if other reactions take place in deposition process. Mass spectroscopy measurements have shown the dissociation of the monomers /3,4/ but it was difficult to be sure that the different species were created by the dissociation in the plasma phase rather than in the mass spectrometer quadrupole. Moreover, the knowledge of the experimental values such as dissociation rate, life time and energy of dissociation is of great importance for the understanding and the modeling of film growth. Another diagnostic technique is the Fourier transform infrared spectroscopy (FTIR). It has been used here to study the dissociation of TEOS and HMDS monomers in a LF plasma. The main variable parameters were the gas pressure and LF power level. That was the preliminary work before a FTIR spectrometry study of an organosilicon multipolar microwave plasma excited by distributed electron cyclotron resonance at low pressure (≈ 1 mTorr). Some authors have reported Fourier Transform Infrared spectroscopy or Infrared Diode Laser spectroscopy diagnostic achieved in RF plasma with less complex gases such as SiH_4, CH_4 /5,6/.

EXPERIMENTAL

Fig. 1 shows the experimental setup used in the present study to record the absorption spectra of the plasma phase. The plasma reactor was a pyrex cylindrical cell (25 mm internal diameter, 100 mm long) closed with two stainless steel flanges. A KBr window was mounted on each flange. Each electrode (steel flange) was connected to the power supply (2,5 khz, 30 watts max). In such a system the residual gas pressure (about 10^{-3} Torr) was achieved with a primary pumping unit. This system was put into the sample compartment of the digilab FTS 6OA FTIR spectrometer. This optical bench was dry-air purged which made the background very stable. The following experimental arrangment was used for the 400 - 4000 cm^{-1} spectral range analysis: DTGS detector, KBr beamsplitter, watercooled high temperature source providing high energy flux density (140 mW) in the beam and leading to a good sensitivity. This spectral range is particularly interesting as it correspond to the vibrations of species such as SiOSi, CH, CH_2, CH_3 and CO. The spectra were recorded with 4 cm^{-1} resolution ; 1 scan was required for each measurement to reduce the measurement time (< 1 sec) and to avoid the problems connected with the SiO_x deposition on KBr windows during plasma phase analysis. The IR beam was focused in the entrance aperture of the DTGS detector after being passed through the optical bench and the gas cell. The background spectrum was measured (residual pressure in the cell $\leq 10^{-3}$ Torr) and then the absorption spectrum of the gas phase, followed by the absorption spectrum of the plasma phase. The absorption pathlength being 100 mm, the concentration of the absorbant species is about 10^{15} at /cm^3 at 30 mTorr. The experiments were carried out at 15 - 40 mTorr with a LF power of 0-30 watts (low power level = limit of plasma ignition, high power level = 30 watts). TEOS and HMDS (Merck) were used as received without any distillation procedure.

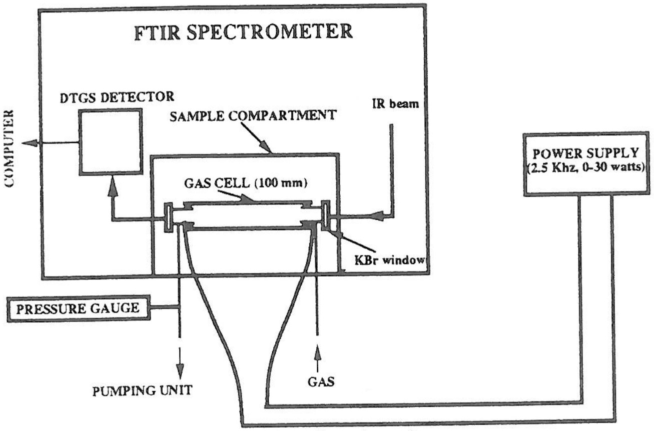

Fig.1 : Experimental setup.

RESULTS AND DISCUSSION

Fig. 2 and 3 show gaseous TEOS and HMDS spectra, both recorded at a pressure of about 40 mTorr. The vibrations of gaseous TEOS have been assigned according to the work of MGM Van der Vis et al /7/. Vibration at 850 cm^{-1} has been assigned to the SiO asymetric stretching mode. The vibrations at 799 cm^{-1} and 965 cm^{-1} belong to the CH_2 rocking mode and CH_3 rocking mode respectively. The bands at 1072 and 1114 cm^{-1} have been assigned to CO asymetric streching mode (strong). The bands observed at 1176 and 1259 cm^{-1} belong to the CH_3 rocking mode and CH_2 twisting mode respectively. The CH_2 waging mode or CH_2 twisting mode have been observed at 1393 cm^{-1} and the CH_3 asymetric deformation at 1450 cm^{-1}. The band at 2900 and 2962 cm^{-1} have been assigned to the CH_2 symetric stretching mode and CH_2 asymetric stretching mode respectively.

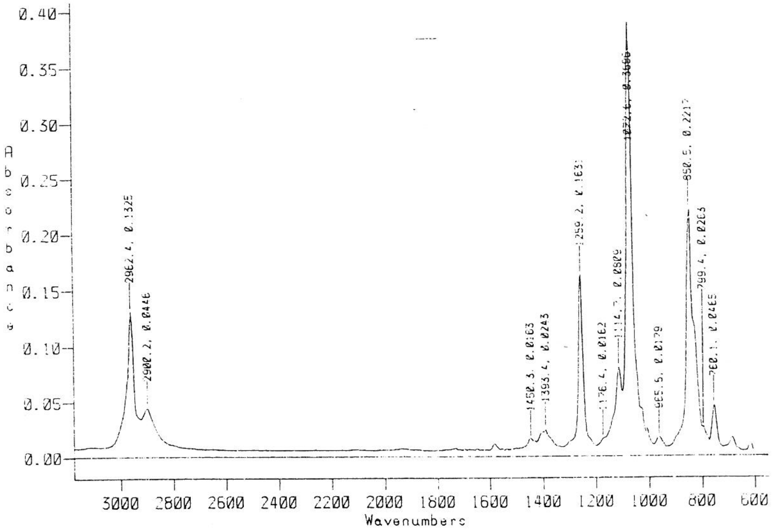

Fig.2 : IR spectrum of gaseous TEOS (plasma off).

The vibrations of gaseous HMDS have been assigned as follows. The vibrations at 759 cm^{-1} has been assigned to the CH_3 rocking mode or to the SiC stretching mode. The vibration at 830 cm^{-1} and 849 cm^{-1} belong to the CH_3 deformation mode. The bands at 1000 - 1100 cm^{-1} have been assigned to the SiOSi asymetric stretching mode. The CH_3 symetric deformation in $(CH_3)_x$ and CH_3 asymetric deformation have been observed at 1261 cm^{-1} and 1414 - 1452 cm^{-1} respectively. The vibrations at 2905 and 2962 cm-1 have been assigned to the CH_3 symetric stretching mode and CH_3 asymetric stretching mode in $SiCH_3$ group respectively.

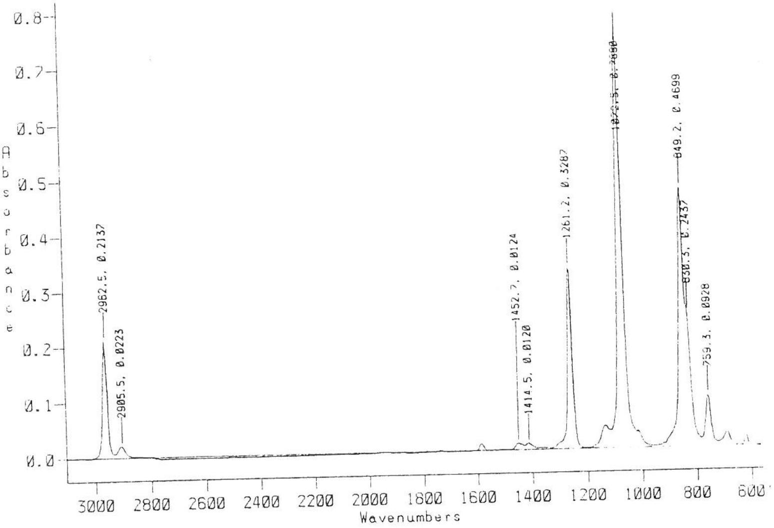

Fig.3 : IR spectrum of gaseous HMDS (plasma off).

At high pressure (40 mTorr) the plasma phase TEOS infrared spectra (Fig. 4) show a gradual decrease with respect to the increase of the LF power. The SiO asymetric stretching mode peak at 850 cm^{-1} is also affected. The peaks at 799 cm^{-1} (CH_2 rocking mode) and 730 cm^{-1} increase and a peak at 3000 cm^{-1} (CH) appears. At lower pressure (fig. 5) the decrease of the peaks occurs from the low LF powers, which is not the case at higher pressure (fig. 4). Moreover peaks at 799 cm^{-1} and 730 cm^{-1} appear at low pressure (fig. 5) for the low LF power then diseappear at higher LF power. A vibration at 780 cm^{-1} appears at high LF power (fig. 5). The 3000 cm^{-1} CH vibration mode appears at low LF power then diseappear at higher LF power (fig. 5). According to these observations, LF power-plasma coupling seems to be more efficient at low pressure than at higher pressure; consequently the dissociation of the monomer molecules is more efficient at low pressure.

Here two hypothesis become apparent. The first one considers that all the peaks decrease with increasing LF energy, owing to the fact that all the bonds (even SiO) are broken. The second one considers that CH, CO or CC bonds are broken and thus the configuration of the molecules changes and the SiO vibration (850 cm^{-1}) from SiO_4 decrease. In that case the CH vibration from CH_3 or CH_2 free groups may appear. It seems to be the case at high pressure (fig 4) for the LF power range 0-30 watts and at low pressure for low LF power (fig. 5) : appearance of the 799 cm^{-1} and 3000 cm^{-1} vibrations. On the other hand when coupling is very efficient (low pressure, high LF power) (fig. 5) the monomer molecule is highly dissociated thus CH peaks disappear.

In the case of HMDS plasma at high pressure (fig. 6) a lowering of the peaks and a saturation effect are observed : the IR gas vibration intensity/IR plasma vibration intensity ratio remains constant (about 2,5) whatever the LF power. This is probably due to a poor LF power-plasma coupling.

Nevertheless a vibration at 1030 cm^{-1} appears, as well as vibrations at 3000 and 2100 cm^{-1}. At low pressure and high LF power (fig. 7) the peaks totally disappear by the improvement of the coupling. Moreover peaks at 1010, 790, 1180 and 3000 cm^{-1} appear. Taking these facts into account, it seems that the monomer molecules have been partially dissociated and that all the bonds have not been broken in the discharge. Thus the second hypothesis appears to be correct as in the case of TEOS plasma.

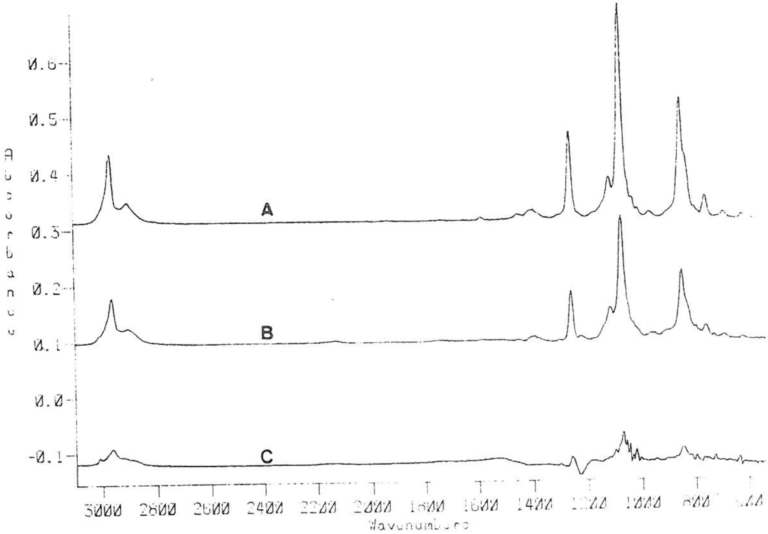

Fig.4 : IR absorption spectrum of TEOS : plasma off(A), plasma on (low power) (B), plasma on (high power) (C), pressure = 40 mTorr.

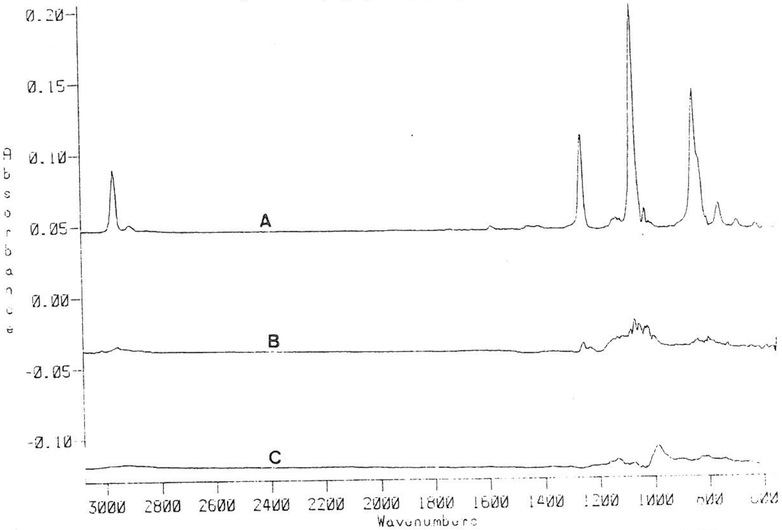

Fig.5 : IR absorption spectrum of TEOS : plasma off(A), plasma on (low power) (B), plasma on (high power) (C), pressure = 17 mTorr.

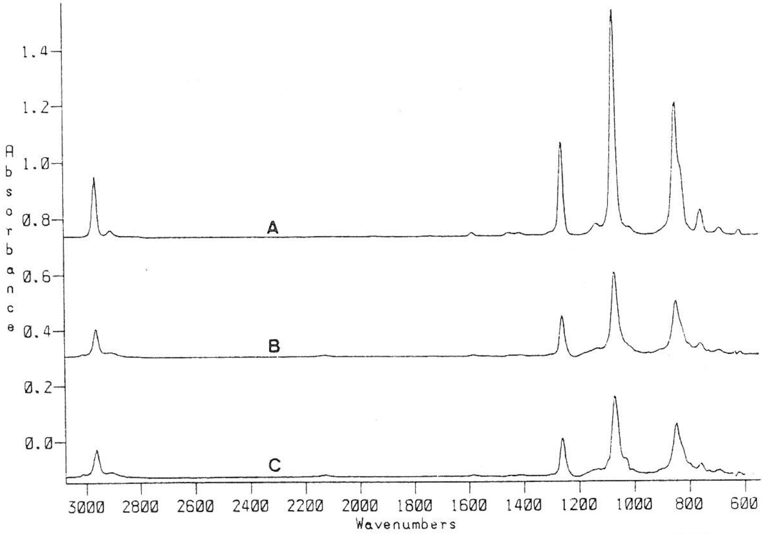

Fig.6 : IR absorption spectrum of HMDS : plasma off(A), plasma on (low power) (B), plasma on (high power) (C), pressure = 41 mTorr.

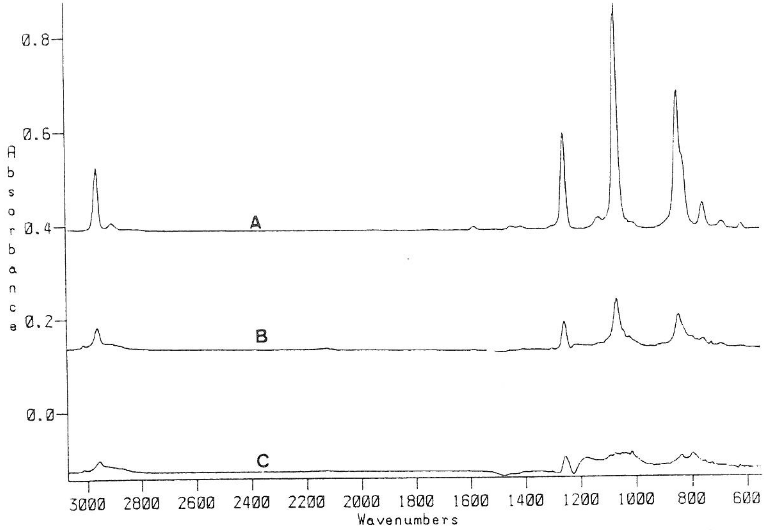

Fig.7 : IR absorption spectrum of HMDS : plasma off(A), plasma on (low power) (B), plasma on (high power) (C), pressure = 27 mTorr.

HMDS plasma and TEOS plasma IR analysis confirms the evolution of the mass spectrometry measurements : Fig. 8 shows the dissociation rate of HMDS and TEOS molecules as a function microwawe power /8/. The TEOS molecules appears to be more easily dissociable than HMDS molecules which is the case in a LF plasma. Moreover the dissociation rate of the HMDS molecule reaches a steady state always lower than the TEOS one, which reinforces this hypothesis.

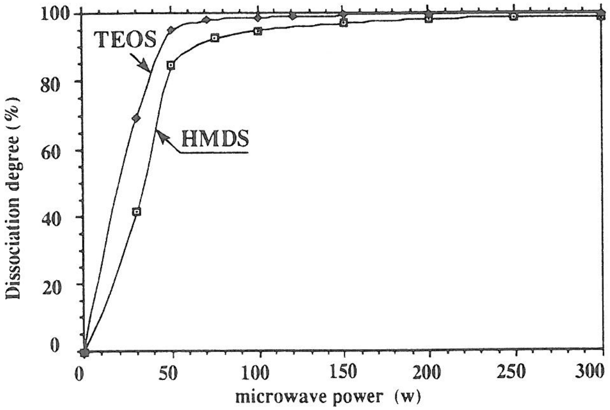

Fig.8 : Degree of dissociation of TEOS and HMDS as a function of microwave power.
Pressure = 0,75 mTorr.

CONCLUSION

Our objective was to study the dissociation of TEOS and HMDS LF plasmas by FTIR spectroscopy. We have shown that the fragmentation of monomers was efficient at low pressure and high LF power (30 watts). Formation of C_xH_y fragments has been observed. Emission spectroscopy measurements achieved in a MMP - DECR reactor /8/ confirm the presence of CH (TEOS, HMDS plasmas) and CO radicals (TEOS plasma).

These infrared analysis of organosilicon LF plasmas have shown that higher sensitivity and higher resolution were required for a better detection of radical formation. Thus the FTIR analysis of TEOS and HMDS multipolar microwawe plasmas will be achieved with a long path white cell and a MCT detector.

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