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Gas Phase and Particle Diagnostic of HMDSO Plasmas by Infrared Absorption Spectroscopy

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ABSTRACT

FTIR spectroscopy has been applied to a radio-frequency discharge in hexamethyldisiloxane (HMDSO) diluted with oxygen and helium as typically used for industrial SiO_x deposition. By measuring the infrared absorption of the HMDSO molecule the gas consumption during processing can be monitored allowing process optimization. Additional information on various infrared active radicals formed within the plasma, such as CO, CO_2 and aldehydes, helps to elucidate the still unknown plasma chemistry in HMDSO plasmas.

Besides information on gaseous components in the plasma, infrared transmission spectra give at the same time important data on the nature of the particle contamination, which is a well-known problem in these plasmas. The particle composition can be determined by fitting the observed characteristic infrared absorption lines from optical constants of appropriate particle materials. Furthermore, in combination with the Mie scattering component of the infrared beam in the spectra, the particle size and particle number density can be determined. The obtained results for the particle size and composition are confirmed by ex-situ electron microscopy investigations and electron energy loss spectroscopy. In addition the shape of the absorption lines allows us to draw some indications on the state of agglomeration of the particles.

INTRODUCTION

Plasma-assisted processes for deposition of silicon dioxide are widely used in industry. Despite the fact that powder formation is observed, only rare reports exist on powder production in RF plasma with HMDSO (hexamethyldisiloxane) as precursor as used in industrial processing of thin film SiO_x. However powder formation has been extensively studied in various silane and silane diluted plasmas [1,2]. The investigations of the present paper aim to increase the understanding of the chemistry and nanoparticle formation in oxygen diluted HMDSO RF plasmas. Practical and robust plasma diagnostic methods are strongly required to understand the plasma physics and chemistry and to optimize the performances of the deposition and its functionality. *In situ* Fourier transform infrared spectroscopy (FTIR) is shown to be a promising diagnostic method for basic research and importantly also for applications in industry. The infrared absorbance spectra contain many informations from different phenomena in the plasma which will be discussed in the following.The aim of this paper is to characterize the HMDSO, oxygen and helium plasmas mixture by *in situ* Fourier transform absorption spectroscopy. The first part shows how to determine the HMDSO consumption from the absorbance spectra [3]. The second part presents a method based on Mie theory [4,5] to determine the radius, number density and the composition of the particles created in the plasma. Finally transmission electron microscopy grid (TEM) and electron energy loss spectroscopy (EELS) results are presented and corroborate the FTIR analysis.

EXPERIMENTAL DETAILS

The experiments were performed in a capacitively-coupled rf plasma reactor operating at 13.56 MHz. The reactor is described in detail in reference [6]. All the experiments, if not specified explicitly were performed with reactor and electrodes at room temperature and at a pressure of 0.8 mbar, controlled by a throttle valve. Typical flow rates are 8 sccm HMDSO, 80 sccm oxygen and 10 sccm helium.

Infrared absorption spectroscopy of the diluted HMDSO plasma was performed by means of a commercial FTIR instrument (Bruker Equinox). The schematic arrangement of the in-situ FTIR diagnostic is shown in Figure 1. The infrared beam leaving the spectrometer is directed through ZnSe windows and the plasma (single pass) and is finally focused by an off-axis paraboloid gold coated mirror onto an external liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Transmission spectra in the range between 700-4000 cm^{-1} with a spectral resolution of

1 cm^{-1} and with an acquisition rate of up to 100 kHz were recorded. To ensure reasonable signal-to-noise ratio, averaging of up to five hundred spectra were usually performed. To minimize the influence of the water vapor and atmospheric CO_2 absorption bands, the infrared light path, including the detection systems, were enclosed and continuously flushed with pure nitrogen gas. Transmission spectra with no gas and no plasma in the reactor were acquired before and after each measurement to check for possible influences of deposited layers on the windows, variations in the sensitivity of the detector and as reference spectra to calculate the absorbance spectra. Mie scattering, using an Argon laser (488 nm) as light source was employed to visualize the powders within the discharge volume.

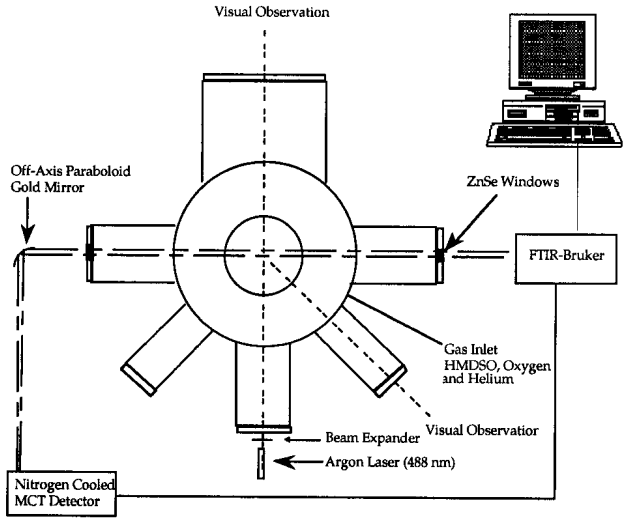

Figure 1 Schematic top view of the infrared absorption spectroscopy (FTIR) arrangement.

The laser beam passing perpendicular with respect to the infrared beam was expanded to illuminate the whole interelectrode gap. In the context of this paper only qualitative visual observations on the powder appearance and behaviour were performed.

The grounded bottom electrode was equipped with a shutter system allowing exposure of copper / carbon grids to the plasma for TEM analysis. This system allowed exposure of the grids either during the plasma or during the afterglow. The grids were then transferred for further investigations to a Philips CM300 microscope equipped with electron energy loss spectroscopy.

RESULTS AND DISCUSSIONS

Figure 2 shows the measured infrared absorbance spectrum for a HMDSO plasma diluted with helium and oxygen.

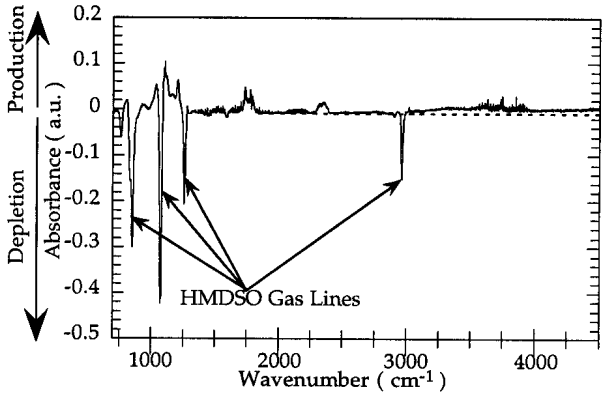

Figure 2. FTIR absorbance spectrum of a highly diluted HMDSO plasma. The plasma parameters: 8 sccm HMDSO, 80 sccm O_2, 10 sccm helium at 0.8 mbar and 40 W.

The absorbance A is obtained directly from the measured transmittance spectra T of the feeding gas and plasma : A= -ln[T(plasma)/T(gas)]. In this representation negative-going peaks indicate a consumption, whereas a positive-going contributions indicate formation or production of solid and/or gaseous matter. The strong negative, narrow band peaks at 850, 1070, 1260 and 2985 cm^{-1} originate from the different infrared active vibrations of the HMDSO molecule [7]. The 850 and 1260 cm^{-1} peaks are attributed to Si-$(CH_3)_n$ vibration ($n \leq 3$), the 1070 cm^{-1} peak to the Si-O-Si stretching, whereas the peak at 2985 cm^{-1} is related to vibration of the methyl group. An overlap between the negative narrow gas peak at 1070 cm^{-1} and a positive broad feature indicates the formation of SiO_x powder within the plasma.

Recently, working gas depletion measurements have been reported for RF silane plasmas [3]. The complex P, Q and R band structure of the silane ro-vibrational absorption spectra induce that particular care must be taken to determine the gas depletion. The absence of any complex band structures in the HMDSO spectra facilitates the gas depletion measurements. In the case of the HMDSO plasma the gas depletion is determined by correcting the transmittance spectrum of the plasma with the gas transmittance spectrum and the absorbance A becomes:

$$A = -Ln\{[T(plasma)/T(vacuum)]/[T(gas)/T(vacuum)]^{\beta}\} \quad (1)$$

where β is chosen to completely eliminate the negative gas peak at 1070 cm^{-1} superimposed on the positive absorption band. It was checked independently that the four main HMDSO gas absorption lines are reduced by the same proportion during the correction. In addition it has been verified that the corrected absorbance is similar to an absorbance spectrum obtained for a helium plasma where SiO_x particles, produced with the same process parameters, have been trapped. The factor $D = (1-\beta)$ is a good estimation of the HMDSO fractional depletion within the plasma. Additional measurements under different plasma conditions have shown that the consumption of HMDSO increases linearly with the power density in the plasma up to a

saturation due to a deficiency of the working gas in the plasma. The saturation is not inevitably equal to a

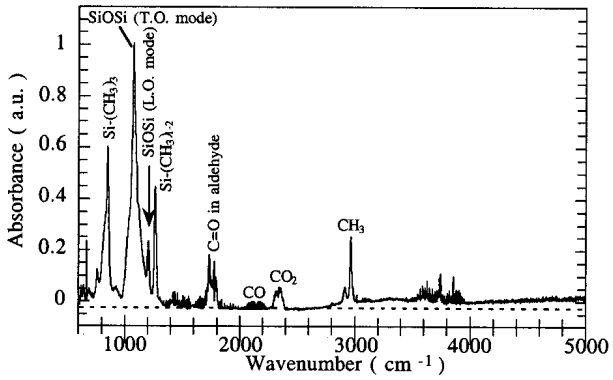

Figure 3. Corrected absorbance spectrum stemming from the elimination of the negative-going HMDSO gas lines in the absorbance spectrum presented in figure 2.

complete depletion of the gas, but depends also on the dilution and the volume occupied by the plasma in the reactor. Figure 3 shows the corrected absorbance spectrum (D≈0.85) of the highly diluted oxygen HMDSO plasma presented in figure 2. Identification of some of the main ro-vibrational lines is presented in table I.

Table I

Frequencies of the absorption bands for the different species created in a HMDSO, oxygen and helium plasma.

Species and vibration type	Frequency (cm^{-1})
Si-O-Si bending	830
Si-O-Si asy. stretch.	1072 (TO) mode
Si-O-Si	1200 (LO) mode
$Si-(CH_3)_{1-2}$ bending	830
$Si-(CH_3)_{1-2}$ sym stretch.	1263
$Si-(CH_3)_3$ rocking	844
CH_3 asy stretch.	2913
sym stretch.	2966
H_2O	1400-1800
	3100-3400
C=O stretch. in aldehyde	1780
CO stretch.	2140
CO_2 bending	667
CO_2 asym. stretch.	2340

The broad emerging structure in the region from 1000 to 1280 cm^{-1} (T.O. mode) [10] indicates the presence of solid SiO_x particles within the plasma. The width of this absorption band is due to the stretch vibration of Si-O-Si linkage [8]. The lines at 844 and 1263 cm^{-1} originate from the rocking and stretch vibrations respectively of $Si-(CH_3)_3$ and $Si-(CH_3)_{1-2}$ respectively. The peak at 830 cm-1 is attributed both to the bending vibrations of SiOSi and $Si-(CH_3)_{1-2}$ respectively. The lines at 2913 and 2966 cm^{-1} originate from the asymmetric and symmetric stretch vibrations of the radical CH_3. Based on the fact that the absorption lines of the HMDSO molecules are completely eliminated by the correction, the remaining $Si-(CH_3)_n$, and CH_3 absorption suggest the presence of carbon compounds within the particles. In higher diluted HMDSO plasma, typically for flux ratio [O2]/[HMDSO] greater than 40 and at a pressure of 0.8 mbar, these absorption peaks disappear, indicating that under this particular plasma conditions only a small amount of carbon is included in the SiO_x particle.

The lines at 2140 and 2340 cm^{-1} represent the gas phase stretch vibrations of CO and CO_2 respectively, whereas the absorption line at 1780 cm^{-1} is most probably due to the C=O stretching in an aldehyde type molecule (R-C=OH), where the radical R is presumably $Si-CH_2$ or CH_3. This measurement clearly shows that in the deposition of SiO_x with the HMDSO molecule, a fraction of the excess carbon is eliminated and transported out of the reactor by the infrared active species CO, CO_2 and by aldehyde formation. Creation of these molecules can be either in the plasma bulk through carbon-oxygen reactions which supposes a fairly high fragmentation of the HMDSO molecule [12] or from plasma-surface reactions such as carbon etching by oxygen of the deposited carbon in the film. The particles are negatively charged in the plasma, chemical reactions on the particles can differ from the reactions on the surface of a substrat, because of different ionic flux and ion energy. The comparison between *ex situ* FTIR measurement on PE substrates with spectra of particles within the plasma shows that significant differences can exist, depending on plasma parameters. The structure and composition of solid phase materials formed in HMDSO plasmas and in SiO_x films is not inevitably the same. The large deviation from the base line, which increases continuously with wavenumber, is attributed to Mie scattering on the nanometer sized particles immersed in the plasma. Detailed analysis of the absorption and the scattering part of the spectra gives additional information about the composition, the size and number density of the particles created in the plasma as will be demonstrated bellow. The absorbance of the infrared beam is given by:

$$\alpha = C_{ext}\, N\, d \qquad (2)$$

where C_{ext} is the total extinction cross section, N the particle number density and d the light path length within the plasma. The total extinction (C_{ext}) of the infrared beam crossing the plasma contains two contributions. The absorption part, which are in our case the Si-O-Si vibrations at 850 and 1000 cm-1 (C_{abs}) and secondly the light scattering part (C_{sca}) on the nanometer sized particles in the plasma. The total extinction cross section is given by the sum of the absorption

and scattering cross sections. In neglecting multiple scattering and assuming spherical particles the scattering and absorption cross sections can be calculated from Mie theory [9] using optical constants for appropriate materials (a-SiO, a-SiO_2, c-SiO_2). The scattering and absorption part of the absorbance spectra depends on refraction index, the wavelength and the particle size. In comparing the absorption peaks of experimental and calculated spectra, information concerning the material composition can be obtained. For particles small with respect to the infrared wavelength (2 to 20 μm), the cross sections C_{abs} and C_{sca} can be given analytically in the Rayleigh approximation [5]. In this case a R^{-6} size dependence for light scattering follows whereas the absorption part shows a R^{-3} dependence. These different dependencies on the particle size allows the determination of the particle size and particle number density.

Figure 4a shows the comparison between the measured absorbance for depletion corrected of a highly concentrated HMDSO plasma (10 sccm HMDSO, O_2 and helium at 0.1 mbar) and the calculated contributions of absorption and light scattering, assuming particles with a radius R_0 of 300 nm. For the present plasma conditions, in regard to the shape of the SiOSi absorption band centered at 1070 cm^{-1}, the best agreement with optical constants

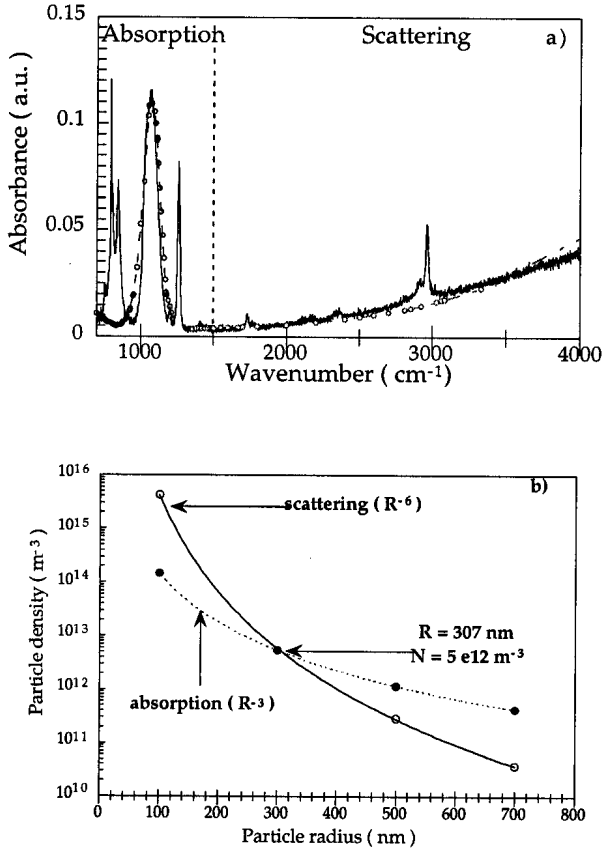

Figure 4. a) Measured absorbance spectrum and calculated absorption and scattering contributions of a highly concentrated HMDSO plasma (10 sccm for HMDSO, oxygen and helium at 0.1 mbar and 40 W). b) Particle size and particle number density estimated from the absorbance spectrum in figure 4a.

from a-SiO material was found whereas in highly diluted plasmas stochiometric a-SiO_2 was found.

Figure 4b shows the resulting particle number densities in fitting individually the measured absorption and scattering absorbance at different particle sizes. An estimation of the particle size and particle number density is obtained at the intersection of the two curves. For the present plasma composition and conditions a particle size of about 600 nm in diameter and a particle number density of 5 10^{12} m^{-3} is obtained. Easy estimation of the most important particle parameters from an absorbance spectra is therefore possible provided that both parts, the absorption and scattering part are used. If the particles are too small, the absorption part is only measured because of its dominant radius dependence. In that case only the volume fraction ($N \cdot R^3$) of the particles can be determined.

In order to cross check the results obtained from infrared absorption spectra interpretation, TEM grids were exposed to the plasma. Figure 5a shows SiO_x particles collected on the grids during the plasma. The assumption of sphericity used for the Mie theory is confirmed by electron transmission microscopy (TEM). The large observed agglomerates are formed from particles with a diameter distribution between 520 nm and 700 nm. Moreover high resolution microscopy (HRTEM) investigations, as shown in the figure 5b, confirms the amorphous nature of

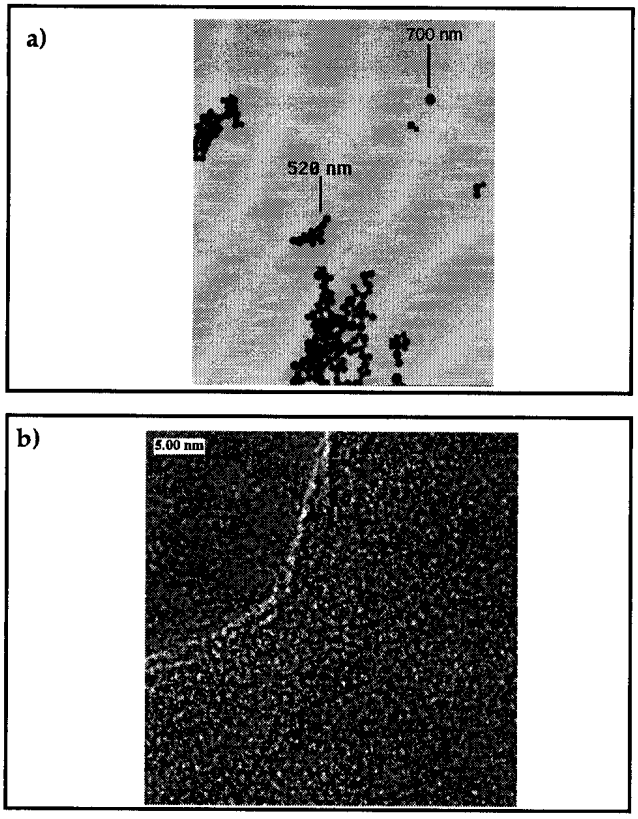

Figure 5. a) TEM picture of agglomerates produced in a highly concentrated plasma. b) HRTEM picture showing an amorphous structure.

the particle structure. Finally electron energy loss spectroscopy (EELS) measurements revealed a O/Si=0.9 ± 0.1 ratio in accordance with the calculation of the absorption peak presented in Fig.4. Moreover additional EELS and HRTEM measurements of powder produced in a highly diluted plasma have confirmed a O/Si=0.4 ± 0.1 ratio and the amorphous structure of the particles.

A continuous rf power HMDSO plasma at high or low dilution produces nanometer sized particles with neck forming agglomerates. To control the size distribution and the agglomeration of these particles a rf power modulated plasma was employed. A highly diluted HMDSO plasma was chosen, which in general shows reduced agglomeration, in order to produced small nanoparticles (<100 nm). Figure 6 shows TEM pictures of particles collected on grids for a continuous (c) and two modulated rf power plasma with 80 ms (a) and 2000 ms (b) of plasma ON time respectively. The OFF time is fixed at 1600 ms, long enough to ensure that the particles are completely spoiled out of the interelectrode space before starting the next discharge. Figure 6a shows that for the 80 ms plasma on case, particles of a few nanometer up to about 40 nm are produced, but no large agglomerates are observed. The infrared absorption spectra shows that the peak of the SiOSi stretching vibrations at 1090 cm^{-1} (T.O. mode) is well separated from the longitudinal optical phonon mode (L.O. mode) at 1200 cm^{-1} [10,11]. Increasing the time ON (figure 6b) increases the appearance of non-spherical agglomerates consisting of

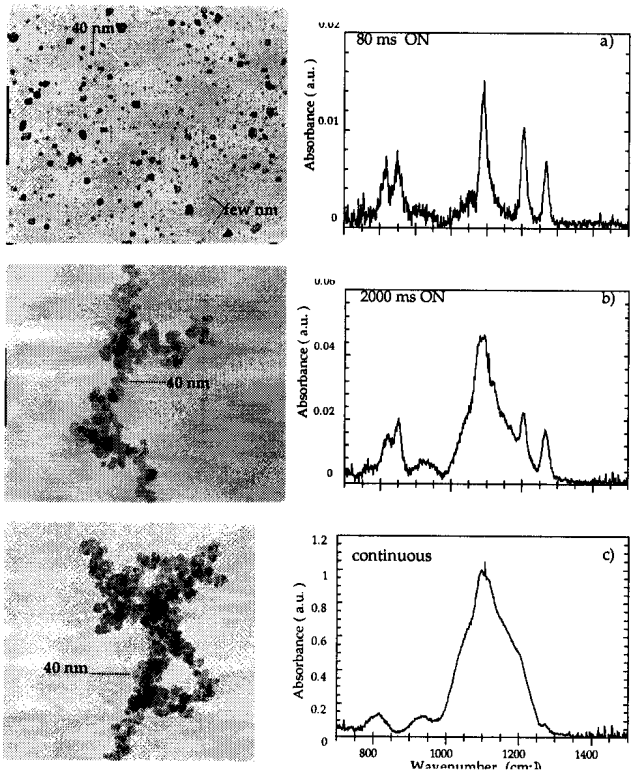

Figure 6. Comparison of absorbance spectra of rf power modulated plasma with TEM pictures of particles produced plasma conditions: a) 80 ms time ON, 1600 ms OFF b) 2000 ms ON, 1600 ms c) continuous rf power discharge.

40 nm diameter monodisperse quasi-spherical particles. In that case total depletion of the HMDSO is observed. The growth of particles saturates presumably due to the radical deficiency in the plasma. The peak centered at 1090 cm^{-1} broadens due to an increase of Si-O-Si linkage number. For the continuous rf power plasma the effect is accentuated, agglomerates almost greater than 400 nm are formed and the so-called (L.O.) mode is completely overlapped by the (T.O.) mode. The broadness of the (T.O.) mode does not allow to distinguish between agglomerates constituted with very large (Fig. 4a) or small particles (Fig. 6). However according to Hu *et al* [11] the vibration line at 1200 cm^{-1} (L.O. mode) becomes active for particles smaller than $\lambda/2\pi n$ ($\approx$360 nm) where λ is the wavelength of the infrared radiation and n the refractive index of the particle ($\approx$2 for SiO). The (L.O.) mode, clearly present in the absorbance spectra of the Fig. 6, is much smaller in the spectrum of Fig. 4 which suggests particle size greater than 360 nm. The TEM picture in Fig. 5a shows 600 nm diameter particles in agreement with the infrared measurement.

CONCLUSION

In situ FTIR measurements were used to investigate HMDSO, oxygen and helium mixture rf plasmas. Useful information can be deduced from measured infrared spectra. Gas depletion during the plasma is estimated by a simple method based on the correction of the transmittance spectrum of the plasma with the gas transmittance spectrum. Absorbance spectra in our plasma conditions reveal loss and produced gas and solid matter. $Si(CH_3)_n$, SiO and CH_x radicals are the main infrared active constituents of the particles trapped in the plasma whereas CO, CO_2 and aldehydes result from the ongoing plasma chemistry. Based on Mie theory the total absorbance cross section of particles trapped in a plasma is fitted to the measured spectra with the radius and number density as parameters and using different optical constants for appropriate material (a-SiO, a-SiO_2, c-SiO_2). In Rayleigh approximation the different radius dependence between the absorption and scattering part of the absorbance spectrum allow us to easily determine the radius and number density of the particles formed in the plasma. Moreover a comparison between the calculated and measured shapes of the absorption of SiOSi vibrations centered at 1070 cm^{-1} gives information about the composition of the particles. It is shown that in highly diluted oxygen HMDSO plasma SiO_2 powders are produced whereas in a plasma at high concentration of HMDSO essentially SiO particles are formed. In addition the absorbance spectra of rf power modulated plasmas show to be a good correlation between the agglomeration state of the particles and the broadness of the SiOSi absorption band (TO mode). Finally the size, composition and the agglomeration state of the particles are confirmed by TEM and EELS results. FTIR absorption spectroscopy appears to be a powerful diagnostic to investigate the radicals and the particles formed in a reactive plasma.

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