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IN-SITU IR ABSORPTION MEASUREMENTS AS DIAGNOSTICS IN PLASMA POLYMERIZATION

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Without any doubt, optical measurements on plasmas are the diagnostic method of the first hour. The overwhelming development in new light sources, optical components, materials and detectors leads to more and more sophisticated optical diagnostics which in turn give access to exciting insights in the physics and chemistry of plasma processing. Besides optical emission spectroscopy (OES) and, since the development of more user-friendly laser sources also laser induced fluorescence (LIF) and other laser-related diagnostic techniques are the most widely used optical methods for temperature and concentration measurements. The (dis)advantages of LIF have been discussed in detail in a previous commentary in this journal [1] In this contribution I would like to discuss the application of absorption spectroscopy in particular in the infrared spectral region to plasma polymerisation.

Besides translational energy, the energy of the molecules (and in plasma polymerisation more and more complex precursors are used), consists of rotational, vibrational and electronic excitation energy [2]. Optical emission and absorption spectroscopy in the visible and UV covers exclusively the electronically exited species whereas vibrational states are excited by mid/near infrared radiation [3]. Since all molecular species, with exception of the homonuclear diatomic are infrared active, IR absorption spectroscopy has wide applicability. However whether a particular molecular species will be actually detected in the plasma depends upon the species concentration, the strength of the infrared absorption and the sensitivity of the spectrometer used. The species that cannot be detected readily by IR absorption technique (atoms, short-lived radicals) are the most easily detected by OES, actinometry, LIF and mass spectrometry, so infrared absorption *complements* these diagnostics.

Different IR sources are available to perform IR absorption spectroscopy. On one side we have IR diode lasers and on the other side the easy to handle Fourier Transform Infrared spectrometers. IR diode spectroscopy allows time, space and high wavelength resolution. The drawback of IR diodes apart from being expensive are the often encountered difficulty of interpretation of crowded spectra. In addition if any other wavelength region (other plasma component) has to be covered, the laser diode has to be changed. FTIR spectrometers are well introduced as a classical material characterisation method and are used to obtain information on the chemical composition of the sample. The broad bandwidth of commercial FTIR spectrometers (400-4000 cm^{-1}) as equipment for in-situ diagnostics has the big advantage to track simultaneously multiple gas species, however at moderate wavelength resolution, moderate sensitivity, and a certain loss of time and space resolution. Other experimental arrangements can cure some of these disadvantages such as for example the cavity ring down configuration which

substantially increases the detection sensitivity at the expense of broad band application. However utilisation of this technique is still difficult since high quality IR optical component are not yet always available for all desirable wavelengths.

In the following I will concentrate on the application of the FTIR spectrometer to the diagnostic of polymerisation plasmas. This diagnostic fulfils many criteria which are important for diagnostics of industrial plasma processing reactors. Diagnostics in this environment should be non-, intrusive, inexpensive, easy to use and handle, and measure in a simple and correct way process relevant parameters. The FTIR absorption spectroscopy easily fulfils most of these demands and turns out to be a very versatile diagnostic, as I would like to show in the following as, FTIR absorption spectroscopy is not only covering information on the molecular components of the plasma but also on powder and radical formation and importantly also on plasma substrate interaction. For successful plasma processing, the relation between reactor relevant parameters and film properties are necessary. However this can only be obtained by in-situ gas and film measurements (plasma and gas composition, gas and surface temperature and film thickness) in order to understand the gas phase and film chemistries; FTIR absorption spectroscopy is a versatile tool for this.

With the help of IR absorption measurements, access to many important process parameters are possible [4]. Monomer depletion partial pressure, detection of plasma created species, and rotational and vibrational temperatures [5] can be obtained. In addition the diagnostic can as well give information on powder formation [6,7] in the plasmas. Combination of emission and reflection/transmission measurement give access to gas and substrate temperature[8]. These in-situ techniques have been applied to many different plasmas processes such as thin film deposition of silicon [8], silicon dioxide [7], and diamond [9], etching plasmas [10] and in plasma polymerisation [11,12].

The extent of dissociation of the gas phase species is an important plasma parameter since the relative concentrations of parent molecules to reactive fragments plays a crucial role in both gas phase and surface reactions. Gas phase IR spectroscopy of reactive plasmas allows detection of the monomer gas(es) and of the most abundant plasma produced molecules and radicals. Determination of the depletion of the monomer has been applied to many different reactive plasmas with various monomers [4,12,13]. Recently the technique has been also been applied to large area industrial reactors [14] where gas consumption is a critical item.

Fig 1 shows the absorbance spectra of plasma produced components of a HMDSO plasma diluted with helium and oxygen. The absorbance is obtained from the measured transmittance spectra of the feeding gas and the plasma. In this representation negative going peaks indicate a consumption, where as a positive going contribution indicated formation of solid and/or gaseous matter. The strong negative narrow band peaks originate from different infrared active vibrations (Si-O-Si, Si-(CH_3)n, CH_3) of the HMDSO molecule. The 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. In Fig 2 the spectrum is corrected for the HMDSO gas depletion (67 % in this particular case). In this case the HMDSO molecule absorption

lines are completely eliminated and the remaining Si-(CH_3)n and CH_3 absorption suggest the presence of carbon compounds within the SiO_x particles. The lines at 2140 cm-1 and 2340 cm-1 represent the gas phase stretch vibration 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. These measurements show that in the deposition of SiO_x with HMDSO, a fraction of the excess carbon is transported out of the reactor by infrared active species CO, CO_2 and by aldehyde formation. Creation of these molecules could be either in the plasma via carbon-oxygen reactions, which supposes a fairly high fragmentation of the HMDSO molecule or from plasma-surface reactions such as oxygen etching of carbon in the deposited film.

Particle contamination of reactive plasmas is at present a very important item and widespread research is going on to understand the powder formation. The infrared absorption technique can also contribute to the comprehension of this interesting phenomenon. In the absorbance spectra shown in Fig 3a the large deviation from the base line is due to elastic scattering on the nanometer sized particles suspended in the plasma. The measured absorbance is the sum of two contributions: The absorption part due to the Si-O-Si vibrations at 1000 cm^{-1} and the light scattering part from the particles. The scattering and absorption cross section can be calculated from Mie theory using optical constants for appropriate materials. Fig 3a shows together the calculated absorbance including absorption, assuming a-SiO particles and scattering at particles with an size of 300 nm and the measured spectra. Light scattering shows an R^{-6} dependence, whereas the absorption follows a R^{-3} dependence. These different dependencies on the particle size allows the determination of the particle size and particle number density (Fig 3b).

In addition it turns out that the width of the Si-O absorption at 1000 cm^{-1} [15] gives interesting information on the status of the agglomeration of the particles in the plasma (Fig 4). In a modulated HMDSO discharge (80 ms plasmas on, 1600 ms plasma off time) small, unagglomerated particles have been obtained. The in-situ infrared absorption spectra in these conditions shows well two separated peaks due to the longitudinal (LO) and transverse (TO) mode. Large agglomerations, as typically obtained in a continuously running discharge tends to broaden these peaks, and leading finally to the LO mode being completely overlapped by the TO mode. Moreover it was found that the breath of the TO mode does not allow to distinguish between agglomerates constituted of very large or small particles.

Besides information about the plasma composition (molecules and powder) nearly the same equipment can be used to measure surface plasma interaction. In particular the in-situ emission FTIR gives information about the surface temperature, whereas reflection FTIR leads to the film thickness and film composition. These methods have been applied to the case of the plasma deposition of amorphous hydrogenated silicon[8].

Beside all the different in-situ FTIR measurements in most cases the same equipment can be used for ex-situ analysis of the treated or deposited samples.

Recently hydrocarbon plasmas [16], boron containing plasmas and many other types of reactive plasmas have been investigated by means of IR absorption spectroscopy showing its impressive large field of application.

This and all of the above mentioned multi-purpose diagnostic applications may let us think of IR absorption spectroscopy (and in particular using FTIR equipment) as a sort of "Swiss Army knife" for reactive plasmas diagnostics. However the interpretation of IR absorption spectroscopy is not always unambiguous. Not all possible plasma gas components are infrared active, furthermore the diagnostic only delivers information about the presence of bonding elements. Often a unique identification of the plasma components on the basis of IR spectra is often not at all possible. Other diagnostics suffer from similar drawbacks. In mass spectrometry, the attribution of different masses is often not unique and the complex cracking pattern also does not help to make life easier.
For example the mass 44 in mass spectrometry is commonly attributed to carbon dioxide (CO_2). In the case of a HMDSO plasma the mass spectra shows the presence of the mass 44, therefore interpreted as gaseous CO_2. However, the IR absorption spectra indicates beside the characteristic vibrations of CO and CO_2 the presence of C-O vibrations characteristic for aldehyde (Fig 2). The aldheyde (C_2H_4O) also shows up at the same mass as CO_2 and is therefore also contributing to the measured intensity in the mass spectra. In addition if the IR absorption spectra is calibrated the partial pressures of the different gaseous constitutants can be determined. This simple example shows well that only both diagnostics together can give a realistic picture of the plasma composition of the HMDSO plasma.
From this we learn that the simultaneous use of several diagnostics on the same reactor is necessary to obtain a correct picture of the ongoing processes. IR absorption spectroscopy might be complemented by mass spectrometry, optical emission spectroscopy and/or actinometry. Out of these various measurements and with the patience of a detective a consistent picture of the investigated reactive plasma can be obtained.
In my opinion, future plasma process reactors in research or in production should be equipped, besides basic parameter measurements, with several complementary plasma diagnostics. Their interplay of different diagnostic methods is a necessity for the advance of plasma processing and towards a better understanding of its physics and chemistry.

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Figure captions

Fig 1

IR absorption spectrum of a diluted HMDSO plasma
(5.5 sccm HMDSO, 13 sccm O_2 , pressure 0.1 mbar, RF power 100W)

Fig 2

Absorbance spectrum of a diluted HMDSO plasma (Fig1) corrected for 67 % depletion of the HMDSO vapour.

Fig 3

a) Measured absorbance spectrum and calculated absorption and scattering contributions of a diluted HMDSO plasma
(10 sccm of HMDSO, O_2 and Helium at a pressure of 0.1 mbar and 40W)

b) Determination of the particle size and particle number density (Fig 3b) from the absorbance spectra in Fig 3a

Fig 4

Comparison of absorbance spectra of a RF power modulated plasma and of a continuous plasmas and TEM pictures of particles produced in the corresponding discharges
a) Modulated plasma (80 ms plasma on, 1600 ms plasma off)
b) continuous RF power discharge

Figures

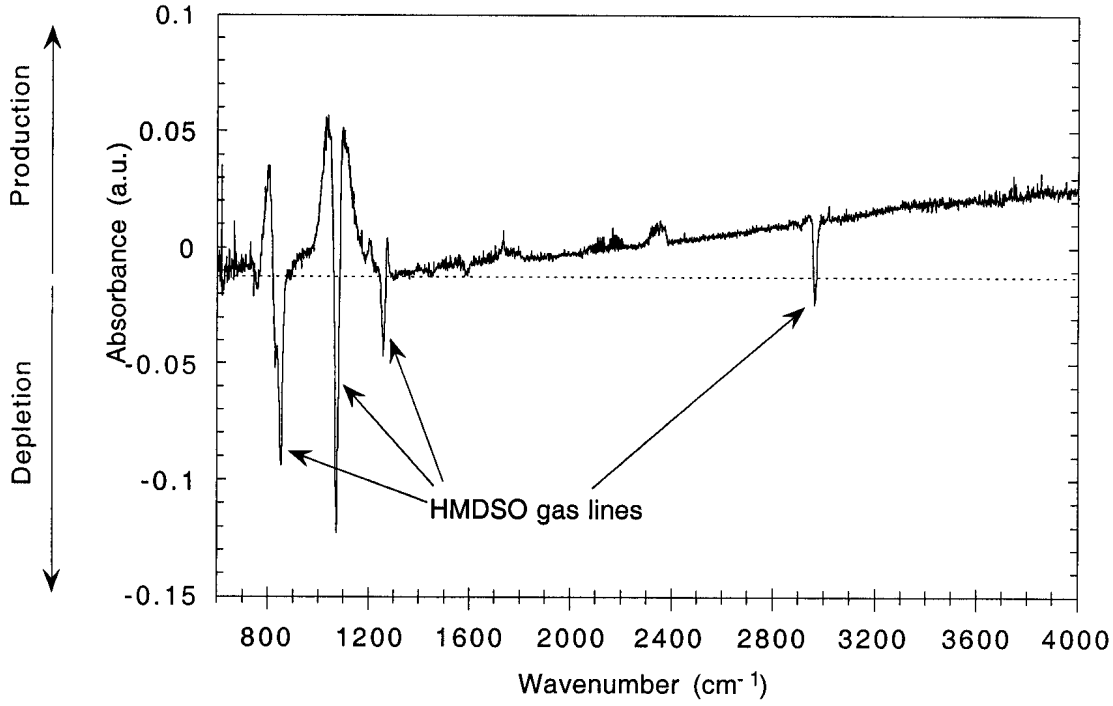

Fig 1.

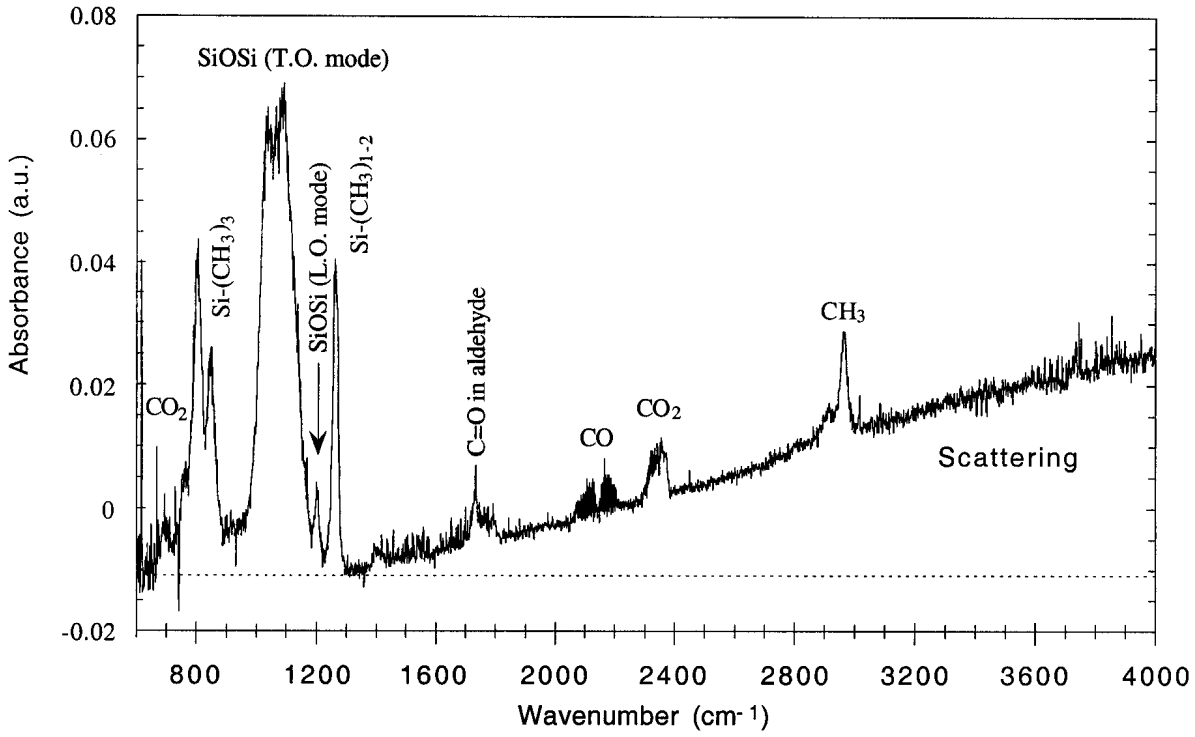

Fig 2

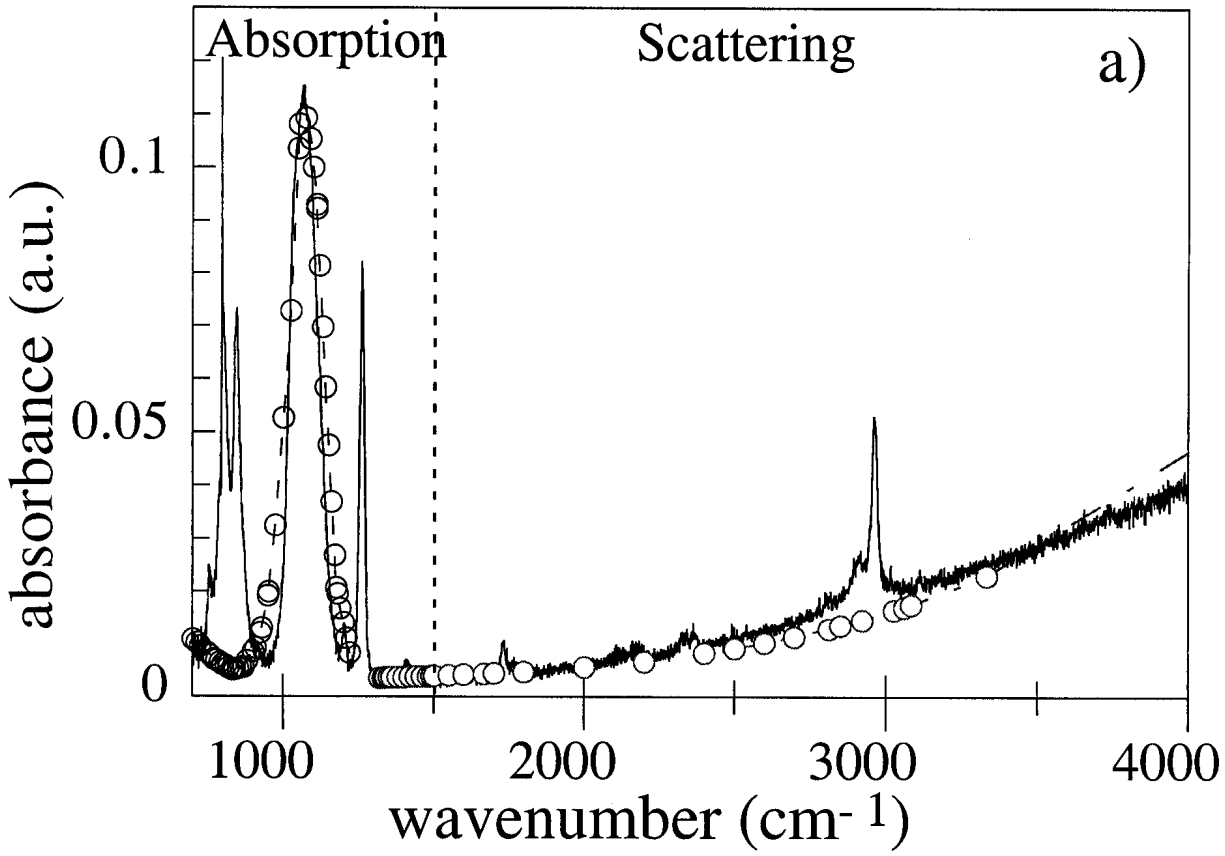
Absorption
Scattering
a)
0.1
0.05
0
absorbance (a.u.)
1000
2000
3000
4000
wavenumber (cm- 1)

Fig 3a

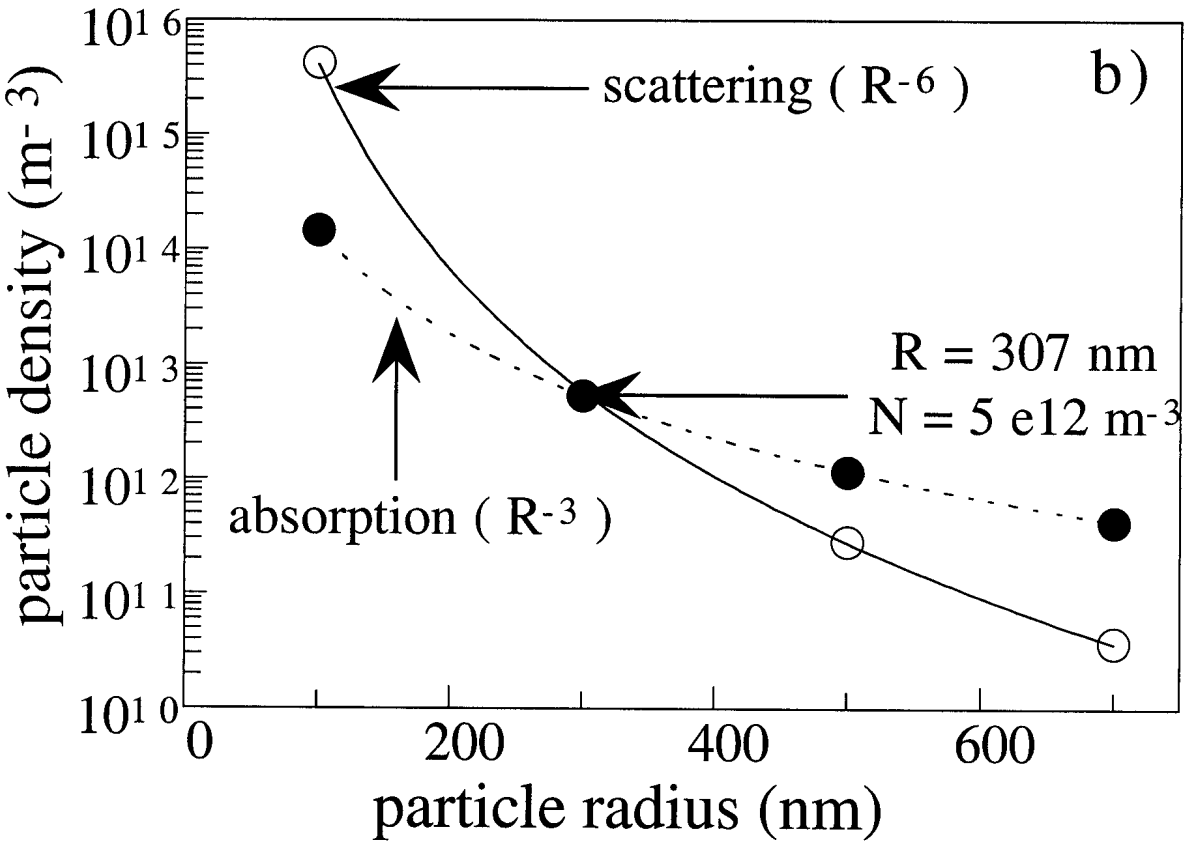
b)
scattering (R-6)
R = 307 nm
N = 5 e12 m-3
absorption (R-3)
particle density (m-3)
10^16
10^15
10^14
10^13
10^12
10^11
10^10
0
200
400
600
particle radius (nm)

Fig 3b

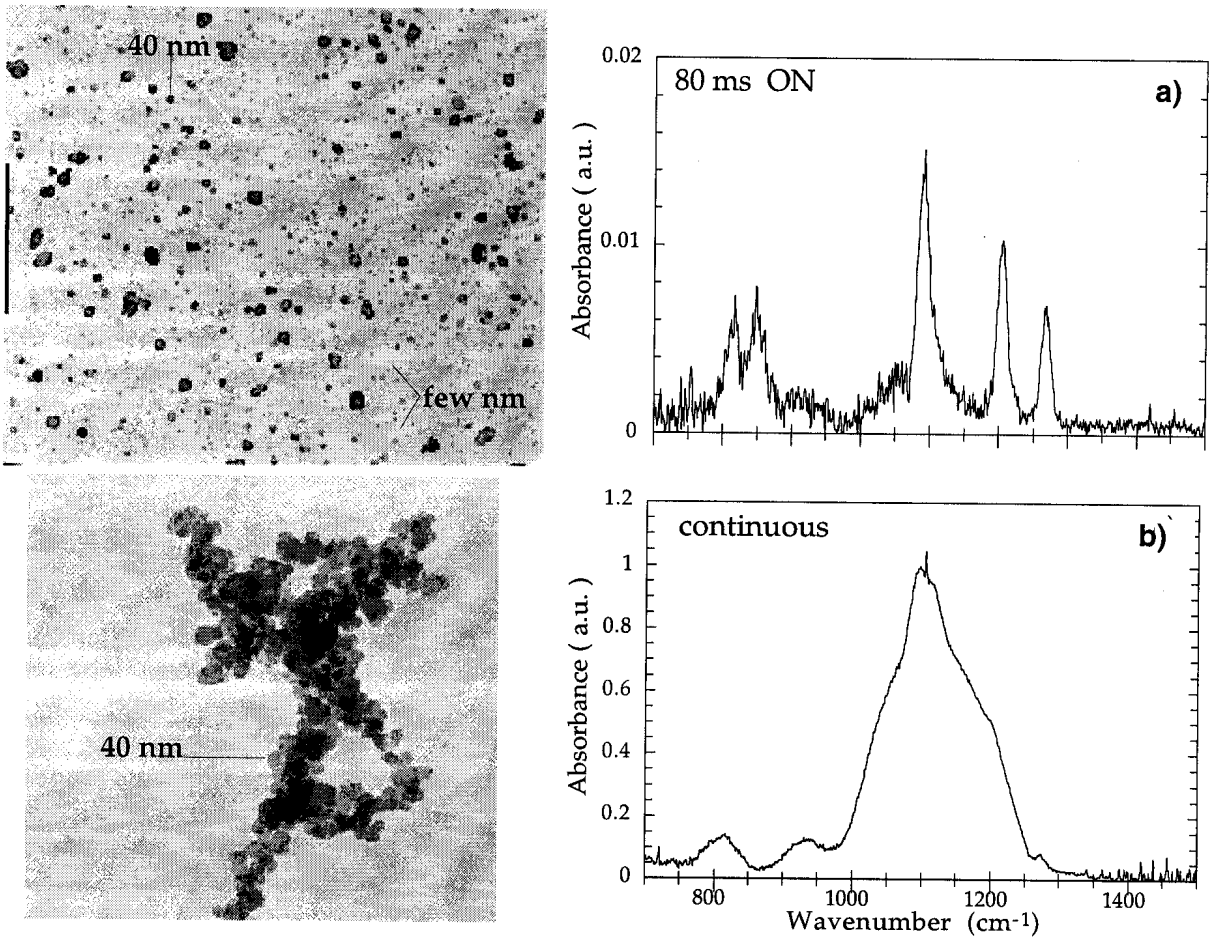
40 nm
few nm
40 nm
80 ms ON
a)
Absorbance (a.u.)
0.02
0.01
0
continuous
b)
Absorbance (a.u.)
1.2
1
0.8
0.6
0.4
0.2
0
800
1000
1200
1400
Wavenumber (cm-1)

Fig 4