In Situ FTIR Investigation of Methyl Methacrylate Plasma, Plasma Polymerized Film and Reaction Mechanisms

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Abstract

This work utilizes *in situ* FTIR (Fourier Transform Infrared Spectroscopy) and *in situ* FTIR/ATR (Attenuated Total Reflection) to investigate methyl methacrylate (MMA) plasma and plasma polymerized methyl methacrylate (PPMMA) film in a capacitively coupled r.f. glow discharge. A statistically designed experimental matrix was carried out by varying the r.f. power, process pressure, and MMA flow rate. Gas phase species were identified, and a reactive intermediate species of MMA is identified as dimethylketene. A gas phase reaction mechanism is proposed and the relationship between the gas and film data is exploited to identify the deposition chemistry.

Introduction

Plasma polymerization is a complex process with numerous ionization agents. *In situ* diagnostics are essential to understanding the plasma chemistry. Goeckner [1] utilized FTIR to study CF_4 etching plasmas and the gas phase species. For deposition processes larger organic monomers such as MMA are used as the feed gas, and the gas phase reaction can be much more complicated. Mass spectrometry was utilized by G. Akovali, B. Ozden (Orhan), and J. Hacaloglu [2] to study the gas phase plasma reactions of various MMA and styrene mixtures, and they found CO, CO_2, and C_2H_4 as reaction by-products. We used *in situ* FTIR diagnostic tools to study a MMA glow discharge to understand its chemistry and the resulting film properties, such as photoluminescence [3]. A statistically designed experimental matrix was carried out using reactor parameters. Statistical and correlation analysis was performed on both gas and film FTIR data to aid the identification of gas phase precursors of different film functionalities.

Experimental Setup

***In situ* FTIR** The plasma polymerization system is a 13.56 MHz capacitively coupled parallel-plate reactor which has been described earlier [4]. Fig. 1 illustrates the *in situ* FTIR set up and the plasma chamber. The IR beam is passed from the spectrometer, through a 2-inch diameter KBr window and into the plasma. Then the beam is passed through another KBr window on the other side of the chamber to be collected by a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Each

FTIR spectrum is from 700 to 4000 cm^{-1} at 2-cm^{-1} resolution and 500 scans are collected during the 3.1 minute acquisition time unless otherwise specified.

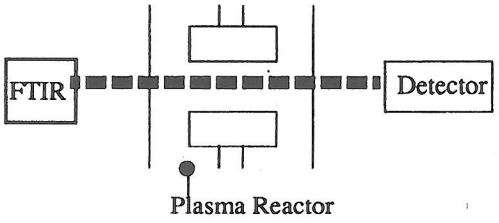

Figure 1. Plasma chamber and *in situ* FTIR set up. The parallel-plate spacing is 3.75 inch.

A statistically designed 2^3 full factorial experiment was performed by varying the reactor parameters between high and low levels: high power=85W, low power=45W; high pressure=300mT, low pressure=100mT; and high flow rate=50sccm, low flow rate=10sccm. MMA was used as received from Aldrich Co. Two sets of substrates (1 glass slide, 1 IR transparent Si wafer chip, 1 non-transparent wafer chip) were placed on both top and bottom electrodes to collect plasma film for later film characterization.

***In situ* FTIR/ATR** As illustrated in Fig. 2, a special assembly is utilized to couple the IR beam from the FTIR into a Ge crystal which is exposed to the plasma as both the substrate and ATR crystal. Gas phase interference was eliminated by purging the assembly with Argon to obtain the pure film spectrum during the plasma deposition. Data collection parameters are the same as *in situ* FTIR, and the three factorial experiment is duplicated to collect the film data.

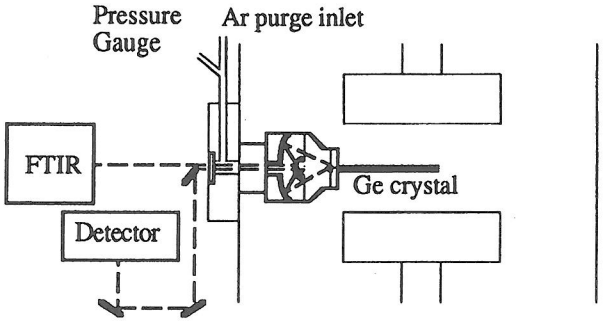

Figure 2. *In situ* FTIR/ATR set up. The parallel plate spacing is 3.75 inch.

Results and Discussion

***In situ* FTIR** There is always some undissociated MMA present during the plasma process, and the resulting spectrum is a combination of MMA and its plasma by-products. Spectral subtraction of pure MMA from the plasma gas yields the spectrum of plasma by-products, and allows an estimation of the extent of MMA dissociation in the plasma. One of the by-products, water, was spectrally subtracted

from the plasma gas spectrum to reduce the spectral interference between 1300 and 1900 cm^{-1}. A subtracted plasma gas spectrum is shown in Fig. 3. A number of gas phase species can be identified from the FTIR spectrum: acetylene, methane, allene, propene, methanol, ethylene, formaldehyde, carbon dioxide, dimethylketene (DMK), carbon monoxide, formic acid, and water.

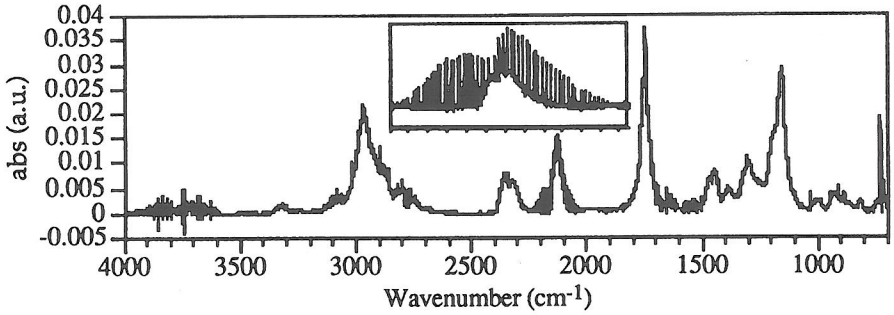

Figure 3. Spectrally subtracted *in situ* FTIR spectrum of plasma at 85W, 300mT, and 50sccm MMA. Insert shows dimethylketene and CO (2000 to 2250 cm^{-1}) from a 0.25-cm^{-1} resolution spectrum.

Different species behave differently under different reactor parameters. However, according to the Beer's Law, the reactor pressure will have a linear effect on the absorption. In order to facilitate the observation of the non-linear effect, absorbance is normalized against the reactor pressure for the statistical analysis. Fig. 4a shows the effect of plasma parameters on DMK and pressure does not have a non-linear effect on DMK. Reactor power and MMA flow rate determine the DMK concentration. As shown in Fig. 4b, DMK has a very similar trend as undissociated MMA percentage in the plasma (correlation coefficent=0.96).

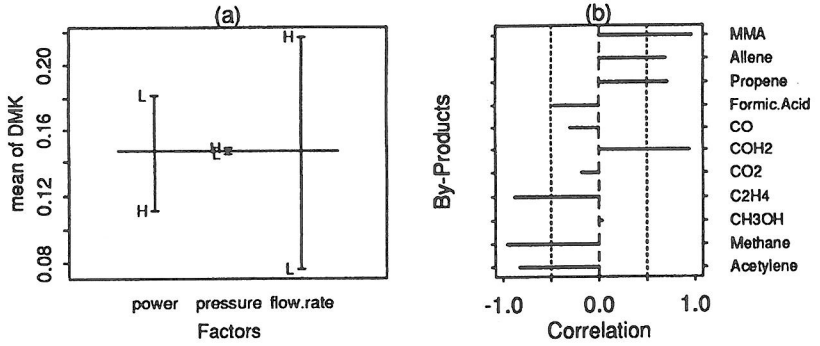

Figure 4. (a) Design plot of the experimental factors on the absorbance of DMK. (b) Correlation coefficient plot of DMK and the different gas phase by-products.

Based on the FTIR data, the following gas phase reaction mechanism is proposed (see Fig. 5). In this mechanism, MMA dissociates to produce DMK and DMK further dissociates yielding other smaller fragments. At the high power and low flow rate setting, greater MMA dissociation is observed and greater DMK production is expected. However, DMK is also being dissociated in the plasma and the observed DMK absorbance reflects only the undissociated DMK. Therefore, the observed DMK concentration is an equilibrium result of MMA and DMK dissociation driven by the plasma condition. Because of the strong correlation between them, the plasma condition seems to have very similar effect on both MMA and DMK.

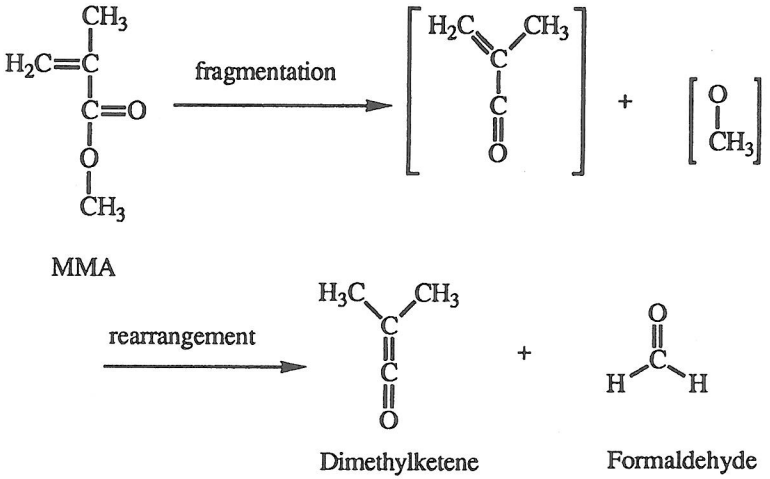

Figure 5. A proposed gas phase reaction mechanism in MMA plasma.

This mechanism is further supported by the significant positive correlation between DMK and formaldehyde (coefficient=0.94) as shown in Fig. 4b. Propene and allene also showed positive correlation coefficients of 0.71 and 0.69, respectively. These larger hydrocarbons are most likely the decomposition products of DMK and MMA when the bond breakage occurred between the carbonyl carbon and the vinyl carbon. Small hydrocarbon fragments, such as acetylene, methane and ethylene are the results of extensive fragmentation of MMA, DMK, and the larger hydrocarbons.

***In situ* FTIR/ATR** The experimental matrix was duplicated to measure the FTIR/ATR film spectrum *in situ*. This technique can also be used to monitor the deposition process in real-time under 'mild' plasma conditions. However, 'hard' conditions can have a significant effect on the Ge ATR crystal and deposited film to obscure the data obtained during the actual plasma deposition. Fig. 6 shows the *in situ* FTIR/ATR spectrum of a PPMMA film and the same film in an Ar plasma (45W, 100mT, and 20sccm Ar flow rate). There is a very clear baseline increase when the Ar plasma is on. Even when this baseline drift is compensated for, there is still more overall absorbance observed from the film. This is probably due to the reflectivity change in the film caused by the plasma because the Ar plasma does not deposit film. However, there is a broad peak around 2100 cm^{-1} in Fig. 6b which is most likely caused by ion bombardment and the creation of C≡C bonds in the film. This C≡C peak

has been observed under all conditions although in different magnitudes. It decreases gradually after the plasma is turned off, an indication of the reactivity between the environment and the C≡C bond or the film in general even in the vacuum chamber.

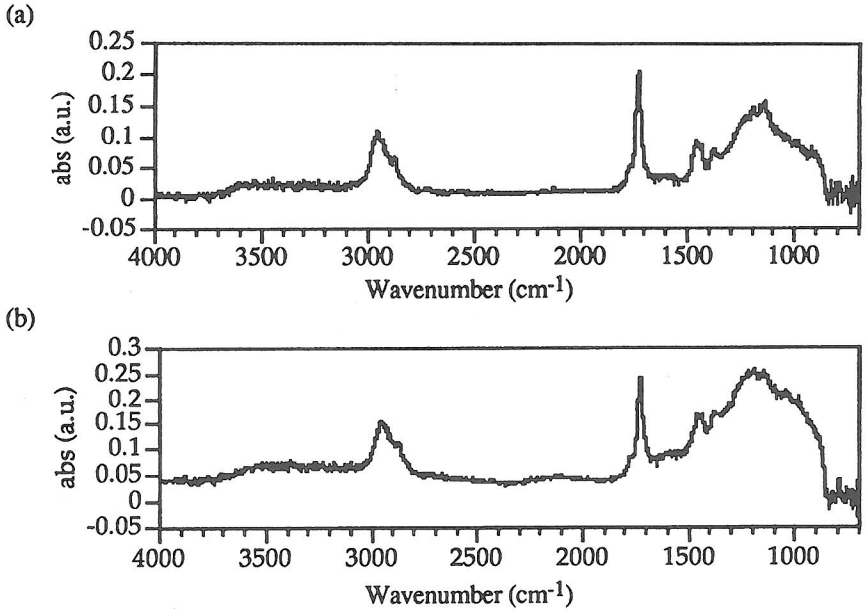

Figure 6. *In situ* FTIR/ATR spectra of (a) PPMMA film; and (b) the same PPMMA film in an Argon plasma. Ion bombardment causes the plasma film to become unsaturated.

Generally, spectra obtained from the experimental matrix have the same peaks but the peaks have different ratios. There are three distinct spectral regions: 850 cm^{-1} to 1500 cm^{-1} (C-O stretching and CH bending), 1650 cm^{-1} to 1800 cm^{-1} (C=O stretching), and 2800 cm^{-1} to 3050 cm^{-1} (CH stretching). Transition in the C-O stretching and CH bending region is difficult to assign because many peaks occur in this region and in the case of PPMMA film only a broad envelope is observed. However, there are two small but distinct peaks at 1370 cm^{-1} and 1450 cm^{-1}, and they are assigned to alkane bending while the large envelope is most likely due to C-O stretching. C-O stretching mode is very sensitive to the environment, such as branching, this envelope indicates that C-O linkages exist in different film environments. In contrast, the carbonyl peak is much better defined and centered at 1731 cm^{-1}. However when compared to conventional PMMA, PPMMA has a full width at half maximum (FWHM) range of 28 to 38 cm^{-1} and PMMA has a FWHM of 23 cm^{-1}. This also illustrates the different environments for carbonyl groups in the film. Furthermore, there is a shoulder at 1770 cm^{-1} which is probably due to the presence of vinyl ester in the film.

From the correlation analysis of gas and film data, the film carbonyl group intensity has the highest correlation with formaldehyde (coefficient=0.74) which also has a carbonyl group. Thus formaldehyde is a possible precursor of the carbonyl group in the film. Other possible precursors include DMK (correlation coefficient=0.66) and MMA which has the highest correlation coefficient with the film carbonyl group (0.48) than any other film functionalities. Thus, at low power and high pressure and flow rate settings, plasma gas has higher concentrations of the three precursors, and the resulting PPMMA films have higher carbonyl group concentrations. The gas phase precursors of the C-O linkage in the film seem to be different from those of the carbonyl group in this analysis. Among the oxygen containing gas phase species, CO_2 and CO have the highest correlation with film C-O linkage (0.75 and 0.66, respectively). At high pressure settings, more CO_2 and CO are produced in the plasma and the plasma film is enriched with C-O linkages. The CH stretching peak has the highest correlation coefficients with the small hydrocarbons such as acetylene (0.73), methane (0.68), and ethylene (0.81), but it has low correlation coefficients with the larger hydrocarbons, such as propene (0.19) and allene (0.08). Therefore, small hydrocarbons, which are present in higher concentration at high power, pressure, and low flow rate settings, contribute most significantly to the CH content in the PPMMA film. Another significant effect of pressure is on the deposition rate. Samples collected on the grounded electrodes were analyzed by profilometer and their thicknesses were dominated by pressure effect (correlation coefficient=0.94) while power and flow rate effects are much less significant (correlation coefficient of 0.29 and 0.16, respectively).

Summary

Different by-products of a MMA plasma have been detected using an *in situ* FTIR diagnostic. Dimethylketene is identified as the intermediate species in the MMA plasma that further decomposes to smaller fragments. PPMMA film spectra were obtained using *in situ* FTIR/ATR. Different film composition of CH, C-O and C=O were observed for different reactor parameters. The gas phase precursors of the different film functional groups were identified with the aid of statistical and correlation analysis of the data from *in situ* FTIR and FTIR/ATR diagnostics.

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