

Plasma polymerization: chemical analysis of the plasma gas phase

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Abstract: The polymerization by radiofrequency (RF) plasma of different monomers (methyl methacrylate (MMA), tetraglyme and 2-hydroxyethyl methacrylate (HEMA)) has been carried out. The plasma gas was investigated by optical emission spectroscopy (OES) in the UV-vis wavelength rang. The excited species formed in the plasma were identified for the different monomers. From computer simulations of the ro-vibration bands, the rotational and vibrational temperatures were derived for the molecular bands of different diatomic excited species. In the tetraglyme plasmas, nitrogen impurity was found, where excited radicals CN, N_2^+ , and N_2 were observed. The vibrational temperatures derived from the analyses of the different emission bands are close to each other ($\approx 3800K$). On the other hand, the XPS surface analysis of deposited thin films did not show any contamination of nitrogen. Correlating information between the plasma gas and the deposited organic thin films is important to understand the physical and chemical processes leading to organic polymer formation by plasma.

Keywords: Polymer, RF plasma, OES, surface characterization, XPS

1. Introduction

Reactive plasma discharge is widely used to modify the surface properties of materials. Plasma processing technology is vitally important to several of the largest manufacturing industries in the world. Recently, new applications, such as fabrication of biocompatible materials, adhesives, low-dielectric constant films, protein anti-absorption coatings, have been carried out by plasma processing. Among thin film polymer deposition processes, plasma polymerization has typical characteristics: almost all monomer can be processed; it is free of solvent; and layer chemical composition is tunable with discharge parameters [1]. For instance, improvement of the retention of the monomer chemical structure has been shown for pulsed discharges [2].

Plasma polymerization is an interesting method for the synthesis of polymers [1], but, is usually performed in an empirical way in view of the large number of free parameters in the complex plasma process. In the plasma deposited polymers fragments and atoms present in gas phase are arranged randomly by a statistic recombination process, so that the real structure of plasma polymers is far from that of their classic analogues. To get some control on the deposition of films it is necessary to understand the plasma processes and the formation of the solid films. Therefore, the investigation of the

plasma gas composition becomes important. This requires knowledge of the electron and ions densities, specie temperatures, and ions energy and flux for given discharge configuration.

A series of investigation of the plasma polymerization parameters has been evaluated with mass spectrometry (MS) – in order to evidence the neutral stable species in the plasma gas, and with optical emission spectroscopy (OES) – in order to evidence the radiative excited stable species and radicals. Since OES allows the detection of short lifetime radicals which are more difficult to detect by MS because of their low concentration, OES appears quite complementary to MS while it is easy to implement. As non-invasive method, the OES technique can provide valuable information on excited atomic and molecular states, and determine the rotational, vibrational, and electronic excitation temperatures of the plasma, thus its level of no equilibrium. In addition, it enables to identify many radicals and active atomic or molecular species and so gives insight in the plasma chemical processes.

Through XPS analyses, the chemical structure of the final polymer films is explored. Certain explication would be given in the context of gas phase dynamics and the reaction kinetics. The correlation of information from the gas phase and the character of

deposited films, it can help to understand and optimize the polymerization.

This paper focuses on the elucidation of the chemistry and mechanism of plasma polymerization with different monomers methyl methacrylate (MMA), tetraglyme and 2-hydroxyethyl methacrylate (HEMA) possess a similar chemical structure and the corresponding polymers are widely used in various biomedical and pharmaceutical components, optical devices, optical lenses, implants, drug delivery systems etc.

2. Experimental

The plasma polymerization was performed in a cylindrical plasma reactor whose design was previously described in detail [3]. The reactor was equipped with an inductively coupled planar radio frequency (RF) source (13.56MHz, ICP-P 200, JE PlasmaConsult GmbH, Germany) with an automatic matching unit.

The total pressure in the chamber is adjusted by varying the microflow controller and by fixing the speed of the primary pump. A pressure meter (MKS-Baratron) measures the actual pressure in the chamber. The reactor is cleaned after a change of monomer, and be pumped until 10^{-3} Pa by turbo molecular pump for 2-3 days before the plasma deposition experiments were performed. Each monomer is heated so that its gas/vapor can be injected by a transport tube terminated by a “shower ring” output, allowing a homogeneous gas distribution in the discharge region of the chamber. When the total pressure reached the set value of 25Pa, it took 15min to wait until the pressure was stable.

The distance between the quartz window of the plasma source and the sample support is 12cm. Before being placed on the sample support, silicon substrates (1cm*1cm) were cleaned in two successive ultrasonic baths of acetone and isopropanol. Deposition time is 8min in each case. Polymer films were deposited at a fixed plasma power of 120W, duty cycle 50% ($T_{on}=0.5$ ms, $T_{off}=0.5$ ms).

The light emitted by the plasma is collected by an optical fibre bundle (25-degree solid angle, 19brins

of 200 μ m) to the entrance slit of the spectrograph. The plasma gas located between the shower ring and the substrate can be investigated. The spectrograph is composed of a 750mm focal length monochromator (Princeton Instruments SP2756A, f/9.7) with 2400, 1800, and 600 grooves/mm gratings that are blazed at 240nm, 500nm, and 300nm respectively. The detector is a 2-dimension cooled CCD one with 1234x400 pixels (Princeton Instrument, E2V CCD36-10). The spectra are acquired by a PC loaded the WinSpec 3.1 acquisition software. Under standard acquisition conditions, the resolution is 0.05nm with 1200 grooves/mm grating. This apparatus allows studying emission lines in the 200-1100nm range with a spectral resolution sufficient for rotational temperature estimate from ro-vibrational band profile fitting. The optical system has been calibrated by tungsten and mercury (argon) lamps.

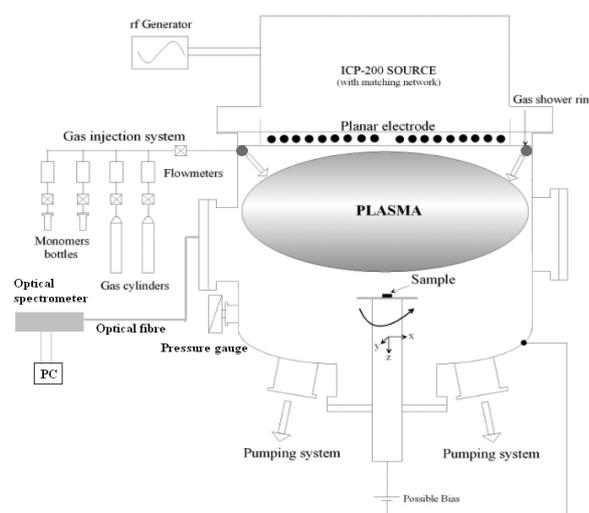


Figure 1. Schematic of the apparatus used.

3. Results and analysis

Investigation of the plasma gas: OES

The typical emission spectra of the 3 different monomer discharges are shown in Figure 2 and Figure 3. At least ten systems of carbon monoxide (CO) dominate the emission spectra on the whole wavelengths range with overlap each other; other excited species observed are O₂, H, H₂, H₂O, CO, and C; a continuum appears in the wavelength rang of 350nm-650nm. The CN, N₂ and N₂⁺ transitions were only observed in the tetraglyme plasma gas,

because of the impurity in the reactor or in monomer liquid (Figure 2).[4-6] The species observed for the different monomer plasma gas are almost the same, but the relative intensity of the excited species or radicals varies with the monomer.

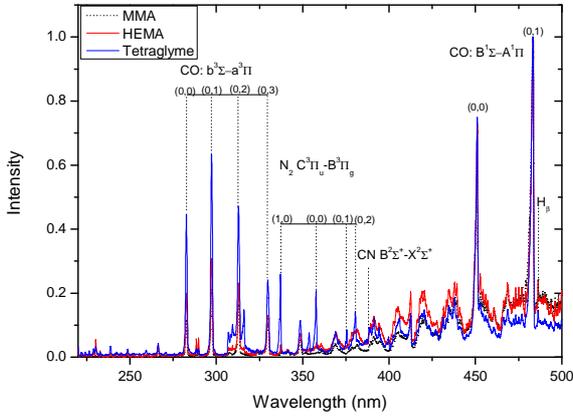


Figure 2. Typical emission spectra in UV region

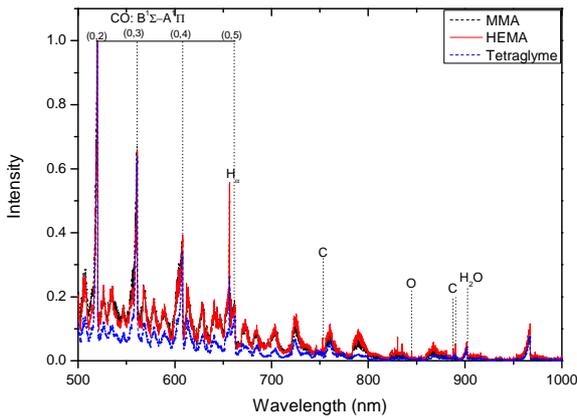


Figure 3. Typical emission spectra in Vis-NIR region.

Spectra of the N_2 2nd positive system ($C^3\Pi_u-B^3\Pi_g$) are the most convenient for plasma diagnostics, since they enable to determine the rotational (T_r) and vibrational (T_v) temperature by fitting the experimental spectra with simulated ones. If this impurity can be seen as the admixture into the plasma, we can use the N_2 band to estimate the plasma parameters. Other radiative excited species can be used for this purpose, like CN or N_2 . The LIFBASE software was used for CN and N_2^+ spectral simulation [7]. The N_2 2nd positive system was calculated by our programme. The relative heights of two band heads (N_2 2nd positive system) with different initial vibrational quantum number are sensitive to T_v . A vibrational temperature $T_v > T_r$

indicates the non-equilibrium in the plasma, although it may not be well defined in strongly non-equilibrium condition when vibrational state does not follow the Boltzmann distribution. The temperature measured from the 3 ro-vibrational band systems of excited species was shown in Figure 4. Owing to fast collision relaxation, the gas temperature T_g equals to T_r . T_r from this simulation is very different of T_r obtained from CH band of the styrene plasma under the same conditions. The farther study is in progress.

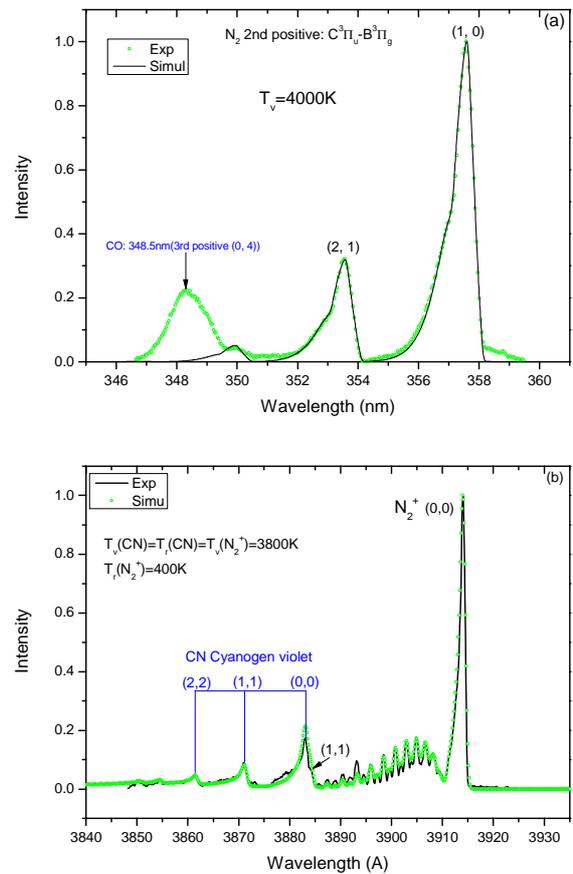


Figure 4. Measured spectra and corresponding best fit modeled spectra at (a) N_2 357.5nm, (b) CN 388nm and N_2^+ 391nm.

Characterization of surface: XPS and ToF-SIMS

The atomic composition of plasma polymerized films was analyzed by XPS. A carbon band around 284.6eV and oxygen around 532eV appear in the XPS spectra. Nitrogen observed for the tetraglyme plasma gas was not detected. The atomic concentration was listed in the Table 1. The concentration of O in the surface increases with the oxygen fraction in monomers. However, due to the

monomer fragmentation in the plasma, the chemical composition of the films was different from their convent structures. The XPS spectra with higher resolution about C1s were analyzed for the 3 types of polymer. The C1s signal shows 3 peak components: C-H or C-C at 285ev, C-O at 286.5ev and C=O at 288eV. According to the fitting attributions, the component C=O that is not found in its monomer appears in the tetraglyme polymer.

Table 1. Characteristics of plasma polymerized films.

| | Concentration (%) | |
|-------------|-------------------|-------------|
| | C1s (284.6eV) | O1s (532eV) |
| PMMA | 89.14 | 10.86 |
| PHEMA | 73.76 | 26.23 |
| PTetraglyme | 69.65 | 30.35 |

The 3 types of polymer deposited by plasma under the same condition were characterized by ToF-SIMS. The intensity is quite large in the low mass region. From the literature data and the monomers structure, the recorded peaks at $m/z = 15, 27, 29, 41, 43, 55, 57, 69$ and 71 are assigned to CH_3^+ , C_2H_3^+ , CHO^+ , C_2HO^+ , $\text{C}_2\text{H}_3\text{O}^+$, $\text{C}_2\text{H}_3\text{O}_2^+$, $\text{C}_2\text{H}_5\text{O}_2^+$, and $\text{C}_4\text{H}_5\text{O}_2^+$ characteristic fragments of tetraglyme, MMA and HEMA [8] [9] [10]. In the tetraglyme polymer film, the mass constituted of nitrogen wasn't also observed, and C=O functionality was significantly found like the XPS spectre.

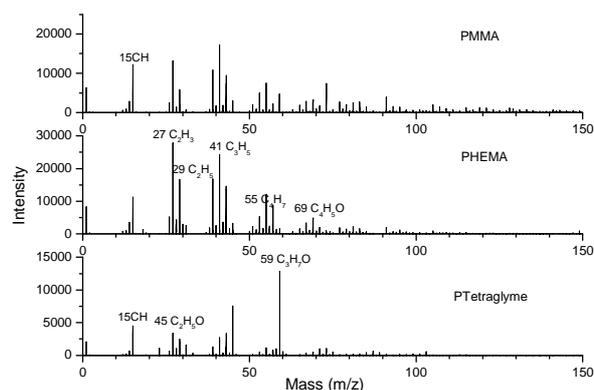


Figure 5. Positive ToF-SIMS spectra for 3 types of polymer films.

4. Conclusion

The species identified in plasma gas were not directly be detected on the surface of the polymer films. CO molecule that dominates in the plasma gas appears in the surface as new functionalities: C=O or

C-O, so the complex reaction (recombination, collision, etc.) happen before the formation of the polymer films. On the other hand, the data for complex molecules of OES is lack, so some species in the spectra of OES which can be trapped in the surface, can't be identified in plasma gas.

Acknowledgments

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