STUDY OF THE CHEMICAL REACTIONS ON LOW PRESSURE RF EXCITED DIGLYME PLASMAS USING MASS SPECTROMETRY AND OPTICAL SPECTROSCOPY


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Abstract

This paper deals with the study of the fragmentation process of \( \text{CH}_3\text{O} (\text{CH}_2\text{CH}_2\text{O})_n \text{CH}_3 \) diethylene glycol dimethyl ether (diglyme) molecule in low pressure RF excited plasma discharges. The study was carried out using actinometric optical emission spectrosocopy and mass spectrometry. The optical spectra were obtained with a monochromator operating in the wavelength range from 250 to 800 nm. The mass spectra were collected by a mass spectrometer operating in the mass range from 1 to 300 amu. Plasmas were generated within a stainless steel cylindrical reactor in a plane parallel plate configuration. The 13.56 MHz RF power was coupled to the chamber through an appropriate matching network. Mass spectrometry allowed one to follow the trends of several chemical species resulted from diglyme molecule fragmentation for different values of pressure and RF power. The results showed that for a fixed pressure, the increase of the RF power coupled to the plasma chamber from 5 to 45 W produced a plasma environment much more reactive which reduces the population of the massive species and increases the population of the lighter one. This fact may be attributed to the increase of the electronic temperature that makes predominant the occurrence of inelastic processes that promotes molecular fragmentation. These results suggest that if one wants to keep the monomer’s functionality within the plasma deposited films resulting from such kind of discharges one must operate in low power conditions. The results obtained for CH, CO, O and H species from actinometric optical emission spectrosocopy show that the relative concentration increases with the increasing of RF power coupled to the plasma discharge, for a fixed value of pressure. These results are in close agreement with the obtained from mass spectrometry. This suggests that the use of actinometry for monitoring the trends of different chemical species is very effective in spite of the inherent simplicity of the method. The results validate the use of this technique as an efficient tool for plasma diagnostics.

Keywords: Molecular fragmentation, Mass spectrometry; Optical spectroscopy, Diglyme plasmas

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1. INTRODUCTION

Plasma materials processing by low pressure RF excited glow discharges is of key importance in many current technological issues encompassing microelectronics and biomaterials industry [1-8]. The main reason is that within such kind of plasmas electrons may attain an energy excess of some eV in comparison with the heavy particles present in the
discharge. This unusual thermal non-equilibrium situation is extremely profitable in molecular fragmentation by electronic impact, giving rise to a very reactive chemistry in a relative cold environment [1-3] whose kinetics is not easily controlled. Therefore is of paramount importance to set many plasma diagnostics in order to probe the trends of chemical species as well as the electrons for different plasma parameters such RF power coupled to the plasma chamber, gas pressure, gas flux and so on [9-12].

In the field of biomaterials science, plasma polymerized poly-ethylene glycol dimethyl ether is a material that has been keeping the attention of the scientific community due to its non fouling characteristics [13-16]. If the appropriate plasma parameters are set these films may be synthesized keeping a molecular structure similar to the polyethylene oxide-like (PEO-like) with the advantage that these films are not soluble in water. The aqueous solubility of PEO makes it less appropriate for many biomaterials applications. In order to retain the monomer structure within the plasma deposited films and consequently its functionality, many different issues have been addressed in recent literature as for instance the film deposition under low mean RF power level by controlling the power supply on/off ratio [9,17], the decreasing of monomer residence time and consequently the reduction of its interaction with the plasma environment [17], the cooling of substratum with liquid nitrogen [11], the energy reduction of the ions reaching the substratum [12], and so on.

In order to set the appropriate experimental parameters that would result customized film structures in plasma polymerization of PEO-like coatings this paper deals with the study of the RF power dependence of different chemical species resulting from diglyme fragmentation for different values of the pressure inside the plasma reactor. The trends of chemical species were followed by mass spectrometry and actinometric optical emission spectroscopy [9,10].

2. EXPERIMENTAL SETUP AND PLASMA DIAGNOSTICS

The glow discharges were generated by a RF power supply operating in the range from 5 to 45 W in CH₃O(CH₂CH₂O)ₓCH₃ (diglyme) atmospheres ranging from 120 mTorr to 300 mTorr within a stainless steel cylindrical, 210 mm of internal diameter and 225 mm long, parallel plate electrodes plasma reactor. The chamber is provided with eight lateral entrances, positioned at the mid plane between the electrodes, that may be used for setting optical, electrical and mass diagnostics and the low (mechanical pump) and high (turbo-molecular pump) vacuum systems. The vacuum inside the plasma chamber is monitored by pirani™ (thermocouple) and penning™ (inverse magnetron) gauges. The turbo-molecular pump is coupled to the chamber through a gate valve and is used for cleanliness purposes. The pressure is pumped down to 10⁻⁶ Torr, being the chamber purged with argon several times before each running of the experiment. The inner side of the plasma chamber was polished up to the optical quality (roughness of 0.5 microns or less) in order to minimize the retention of impurities and facilitate the cleaning process. The plasma chamber walls were heated with a temperature controlled belt in order to minimize the monomer’s condensation as well as the humidity. Diglyme was placed inside a stainless steel bottle and was fed into the plasma chamber through a needle valve. The plasma was excited by a RF power supply operating in 13.56 MHz whose output intensity could be varied from 0 to 300 W (Tokyo HY-Power model RF-300™). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300™) that allows one to minimize the reflected RF power. The mass spectrometry was performed using a mass spectrometer and energy analyzer (Hiden Analytical model EQP-300™), operating in the mass and energy
range from 1 to 300 amu and from 0 to 100 eV respectively. The optical spectra were collected using a computer controlled 2 m focal distance plane grate spectrometer provided with a photomultiplier operating in the range from 800 nm to 250 nm (Hamamatsu model R374). The block diagram of the experimental setup is presented in Figure 1.

**Figure 1.** Block diagram of the experimental setup used in plasma polymerization of diglyme for different values of pressure and RF power coupled to the reactor.

The spectroscopic method used to study the trends of different chemical species within the plasma is the well known Actinometric Optical Emission Spectroscopy [2,5,9,10]. Briefly it consists in the insertion of an chemical inert gas (Ar, He for instance) or an almost inert gas (N₂) within the discharge in a relative low concentration (no more than 5 %) so that it does not disturb the plasma. The necessary condition for a chemical species to be used as an actinometer is that the threshold for its excitation by electronic impact must be in the same range of energy as the chemical species excitation, whose concentration within the discharge one wants to probe. It is also assumed that the cross section for excitation by electronic collisions of both (the species of unknown concentration and the actinometer) is almost the same assuring that the ratio between the quantum efficiencies of both is approximately cross section independent. If such assumptions are valid, the trends of the chemical species whose concentration within the discharge is unknown may be followed from the knowledge of the actinometer concentration and the measurements of the light intensity emitted by the actinometer and the species [2,5].

**3. RESULTS AND DISCUSSIONS**

It is presented in table 1 all the possible primary fragments of diglyme molecule (134 amu) resulting from the disruption of the chemical bonds between carbon-carbon and carbon-oxygen atoms. Since the molecule is central symmetric to the oxygen atom located in ethylene-glycol group one may identify only four different points of molecular disruption involving the above mentioned chemical bonds which results the fragments listed in Table 1.
Table 1. Primary Diethylene-glycol-dimethyl-ether fragmentation products

<table>
<thead>
<tr>
<th>fragment</th>
<th>chemical structure</th>
<th>mass (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>CH₂O</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>CH₂OCH₂</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>CH₂OCH₂CH₂</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>CH₂OCH₂CH₂O</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>CH₂OCH₂CH₂OCH₂</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>CH₂OCH₂CH₂OCH₂CH₂</td>
<td>103</td>
</tr>
<tr>
<td>8</td>
<td>CH₂OCH₂CH₂OCH₂CH₂O</td>
<td>119</td>
</tr>
</tbody>
</table>

It may be pointed out that all the molecular fragments presented in table 1, with the exception of the number 8 (119 amu), may result from secondary or higher fragmentation process of the more massive fragments of the diglyme molecule. The number of possibilities contributing for the population of a fragment increases inversely proportional to its mass. From the point of view of the non-fouling characteristic of the plasma deposited diglyme films the ethylene-glycol structure, e.g., CH₂OCH₂ (44 amu), is one the most important structure to be retained within the film composition if one wants to keep its functionality [2]. Therefore is important to keep under control the plasma parameters that enhances the presence of massive fragments within the discharge.

![Figure 2. Power dependence of diglyme fragments products at a fixed pressure of 120 mTorr.](image)

Figure 2 shows the RF power dependence of diglyme fragments within the plasma, for a fixed pressure of 120 mTorr. It can be seen that as the RF power coupled to the plasma chamber increases the concentration of the massive species decreases indicating the predominance of electronic inelastic collisions resulting in molecular fragmentation. It also can be appreciated that the concentration of less massive species like CH (13 amu), H (1 amu), and O (16 amu) increases with the increasing of the RF power. This result is in agreement with the decreasing of the concentration of the massive species within the plasma discharge. It is shown in Figure 3 the results obtained at a fixed pressure of 300 mTorr. One may see that the trends of different chemical species are quite similar to the presented in Figure 2. It is seen that only the particle’s count rate increased with the increasing of the pressure from 120 to 300 mTorr. This indicates that the pressure increasing was not enough to
change significantly the electronic mean free path and therefore the electronic mean kinetic energy, that would result the production of different chemical species due electronic inelastic collisions.

![Figure 3](image)

**Figure 3.** RF power dependence of diglyme fragments products at a fixed pressure of 300 mTorr.

Figure 4 presents the RF power dependence of the concentration of lighter species, for a fixed pressure of 120 mTorr, resulting from diglyme fragmentation. The results were obtained through actinometric optical emission spectroscopy.

![Figure 4](image)

**Figure 4.** Power dependence of lighter species resulting from diglyme fragmentation processes obtained by optical emission spectroscopy.

It can be appreciated that the concentration of the species increases with the increasing of the RF power coupled to the discharge. This suggests that the plasma activity is more intense for higher values of RF power. These results are in close agreement with those obtained by mass spectrometry, presented in Figure 2.

4. CONCLUSIONS

One can conclude from the presented results that the operation of the plasma reactor at low RF power levels is appropriate if one wants to preserve the monomer functionality since it enhances the predominance of massive chemical species within the discharge. The results
also showed that actinometry is a powerful method for plasma diagnostics in spite of its inherent simplicity.

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REFERENCES