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Study of RF-excited Diethylene Glycol Dimethyl Ether Plasmas by Mass Spectrometry

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Abstract. This paper deals with the study of the fragmentation process of diethylene glycol dimethyl ether ($CH_3O(CH_2CH_2O)_2CH_3$) (diglyme here in) molecule in low pressure RF excited plasma discharges. The study was carried out using mass spectrometry. The results showed that for a fixed pressure, the increase of the RF power coupled to the plasma chamber from 1 to 35 W produced a plasma environment much more reactive which increases the population of the ionized species like CH_3^+ (15 amu), $C_2H_4^+$ (28 amu), CH_3O^+ (31 amu), $C_2H_4O^+$ (44 amu), $CH_3OCH_2CH_2^+$ (59 amu) and $CH_3OCH_2CH_2O^+$ (75 amu). This fact may be attributed to the increase of the electronic temperature that makes predominant the occurrence of inelastic processes that promotes molecular fragmentation. For a fixed value of RF power the increase of pressure from 50 mTorr to 100 mTorr produces the decreasing of the above mentioned chemical species due the lower electronic mean free path. 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.

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]-[4]. 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 whose kinetics is not easily controlled [2, 4]. 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 [1]-[4]. 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 [5]-[11]. 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 [12, 13], the decreasing of monomer residence

time and consequently the reduction of its interaction with the plasma environment [14], the cooling of substratum with liquid nitrogen [15], the energy reduction of the ions reaching the substratum [16], 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 ionized chemical species resulting from diglyme fragmentation for different values of the pressure inside the plasma reactor. The trends of different chemical species were followed by mass spectrometry [2, 4].

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 diglyme atmospheres ranging from 50 mTorr to 100 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^{TM} (thermocouple) and penning^{TM} (inverse magnetrom) gauges. The turbo-molecular pump is coupled to the chamber through a gate valve and is used for cleanness 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 μm 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 W to 300 W (Tokyo HY-Power model RF-300^{TM}). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300^{TM}) that allows one to minimize the reflected RF power. The mass spectrometry was performed using a mass spectrometer and energy analyser (Hiden Analytical model EQP-300^{TM}), operating in the mass and energy range from 1 amu to 300 amu and from 0 eV to 100 eV respectively. The block diagram of the experimental setup is presented in Figure 1.

3. Results and discussion

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. It must 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 heavy 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., CH_2CH_2O (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 enhance the presence of heavy fragments within the discharge. Figure 2 shows the RF power dependence of diglyme fragments within the plasma, for a fixed pressure of 140 mTorr. It can be seen that as the RF power coupled to the plasma chamber increases the concentration of the ionized species increases indicating the predominance of electronic inelastic collisions resulting in molecular fragmentation. Figure 3 shows a typical

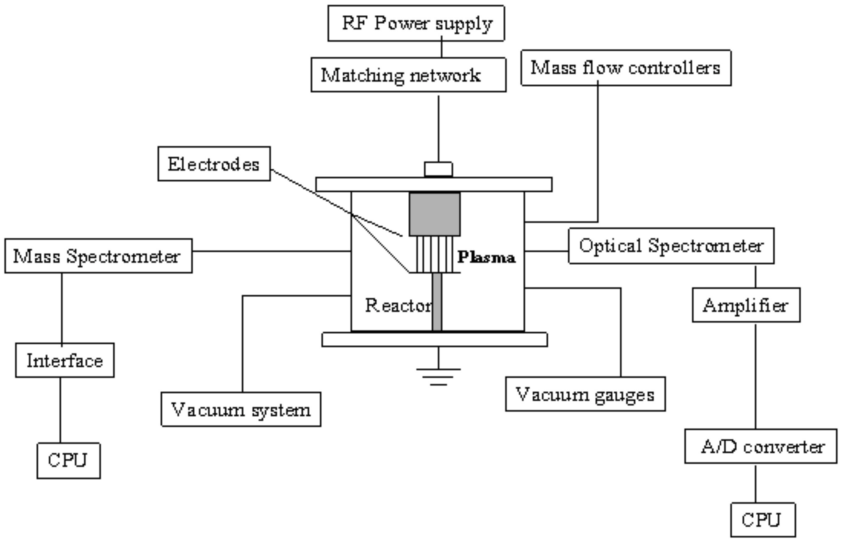

Figure 1. Block diagram of the experimental set-up

Table 1. Primary Diethylene-glycol-dimethyl-ether fragments and the monomer molecule

fragment	chemical structure	mass (amu)
1	CH_3	15
2	CH_3O	31
3	CH_3OCH_2	45
4	$CH_3OCH_2CH_2$	59
5	$CH_3OCH_2CH_2O$	75
6	$CH_3OCH_2CH_2OCH_2$	89
7	$CH_3OCH_2CH_2OCH_2CH_2$	103
8	$CH_3OCH_2CH_2OCH_2CH_2O$	119
monomer	$CH_3OCH_2CH_2OCH_2CH_2OCH_3$	134

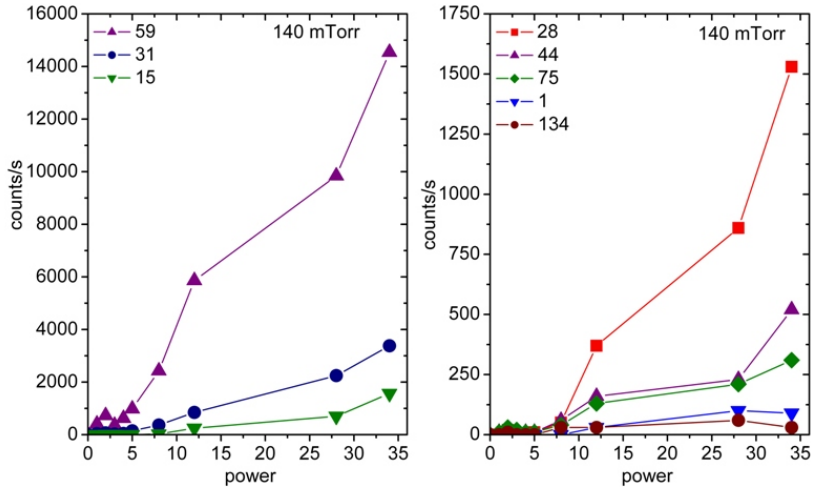

Figure 2. RF power dependence of diglyme fragments for a fixed pressure of 140 mTorr

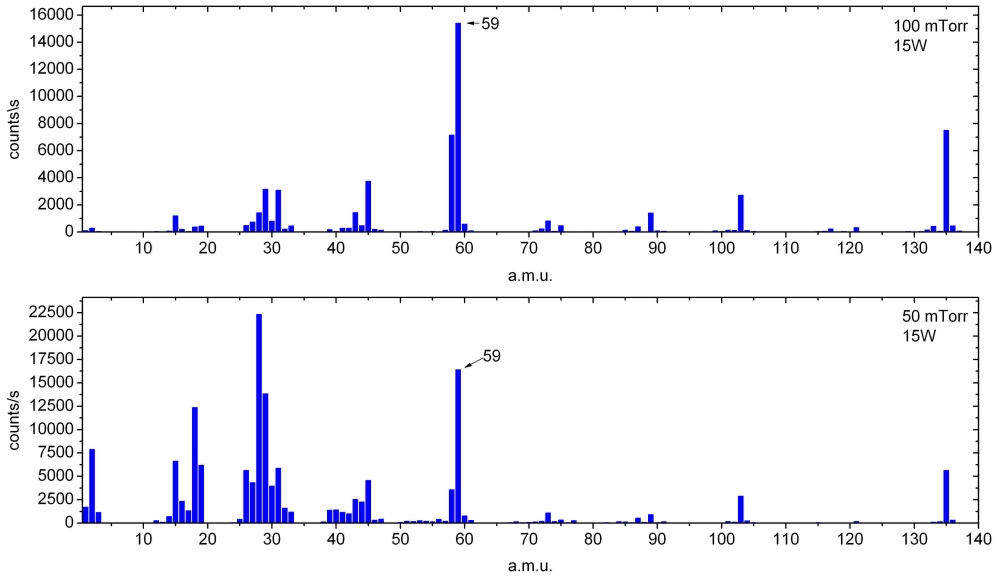

Figure 3. Typical diglyme mass spectra from 1 amu (atomic mass unit) to 134 amu, at 100 mTorr (top) and at 50 mTorr (bottom), for 15 W of RF

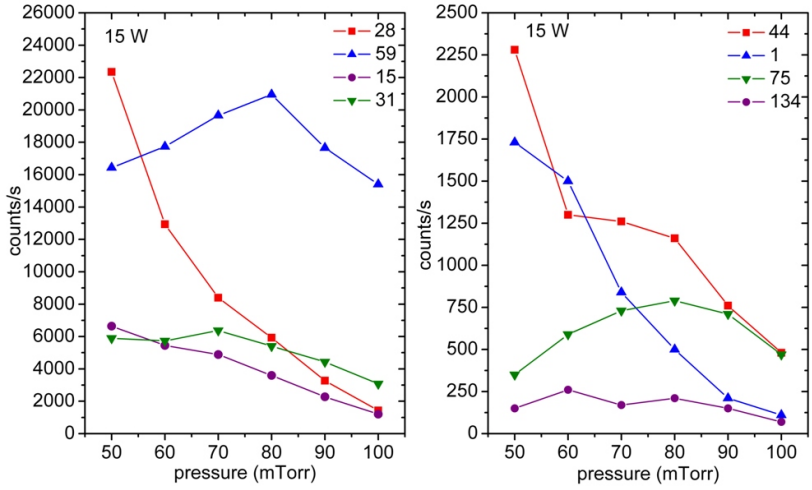

Figure 4. Pressure dependence of diglyme fragments for 15 W of RF power

diglyme mass spectra run at 100 mTorr and 50 mTorr for the RF power kept fixed on 15 W. It may be seen that the number of lighter chemical species increases considerably. This behaviour of discharge can be explained if one considers that for lower pressure the molecular fragmentation is enhanced due the higher values of electronic mean free path and mean temperature. Figure 4 shows the pressure dependence of diglyme ionized fragments for a fixed RF power coupled to the plasma chamber. It can be appreciated that the number of ions decreases with pressure mainly due to molecular recombination process that is enhanced in such conditions. This fact is corroborated by the neutral species mass spectra data, not shown in the present paper.

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 into the plasma deposited thin films, since it enhances the predominance of heavy chemical species within the discharge reducing the fragmentation processes.

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