



Chemical species from diethylene glycol-dimethyl ether/argon discharges investigated at low pressure by mass spectrometry



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ABSTRACT

Mass spectrometry is an important technique to investigate vacuum and discharges maintained at low or high pressure. It has been used to investigate plasma discharges from organic and inorganic gases or vapors. Plasma of organic gases or vapor can produce materials with interesting technological application. In this work, it was used to investigate the plasma discharges from diethylene glycol dimethyl-ether (diglyme)/argon at low pressure. The discharges occurred in a cylindrical stainless steel reactor, excited at 13.56 MHz from 10 Pa to 30 Pa as a function of partial pressure of the diglyme/argon mixture for different radio frequency powers between 1 and 40 W. The species assigned to H⁺ ($m/z = 1$), CH₃⁺ ($m/z = 15$), CHO⁺ ($m/z = 29$), CH₃O⁺ ($m/z = 31$), CH₂CH₂O⁺ ($m/z = 44$) and CH₃OCH₂CH₂⁺ ($m/z = 59$) were investigated. The molecular structure of the films produced from these plasmas was analyzed by FTIR spectroscopy technique presenting C–O; C–O–C; C–H; C=C and O–H bonds.

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1. Introduction

Material processing using low-temperature/pressure AC/DC excited plasmas is of key importance in many current technological issues encompassing microelectronics, mechanics, coatings and biomaterials, among other industries [1–14]. The main reason is that within such 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 scenario is extremely profitable in molecular fragmentation by electronic impact, giving rise to a very reactive chemistry in a relatively cold environment that kinetics is not easily controlled [1–10]. Therefore, it is of paramount importance to set many plasma diagnostics in order to probe the behavior of the chemical species as a function of the AC or DC power coupled to the plasma chamber, gas pressure, gas flux and so on [1–4,8]. In the field of biomaterials, plasma polymerized diethylene glycol dimethyl ether (diglyme) – CH₃OCH₂CH₂OCH₂CH₂OCH₃ – is a material that has been keeping the attention of the scientific community due to its non-fouling characteristics [15–26]. If appropriate plasma parameters are set, these films may be synthesized, keeping a molecular structure which is similar to polyethylene oxide (PEO), so called as

polyethylene oxide-like (PEO-like), with the advantage that these films are not soluble in several liquids and resistant to acids and bases. The aqueous solubility of PEO makes it less appropriate for many biomaterials applications. In order to retain the monomer functional group that generate a PEO-like structure within the plasma deposited films and consequently its functionality, many different issues have been addressed in recent literature, e.g. the film deposition under low mean RF power level by controlling the power supply on/off ratio [26,27], a decrease in monomer residence time and thus a reduction of its interaction with the plasma environment [23,27], cooling the substrate with liquid nitrogen [28], an energy reduction of the ions reaching the substratum [29], and so on. In order to set appropriate experimental parameters that would result in a customized film structure in plasma polymerization, this paper deals with the study of the RF power and pressure conditions dependence on different ionized species, resulting from diglyme fragmentation into diglyme/argon discharges. The behavior of different chemical species was followed by mass spectrometry [2,4]. Argon was used to contribute to the system cleaning process and in the diglyme/argon mixture to investigate the plasma and the deposition processes.

The molecular structure characteristics of plasma films deposited on aluminum substrates at 5 W and 15 W (RF power) and operated at 13.3 Pa total pressure using different proportions of diglyme/argon were characterized by FTIR measurements.

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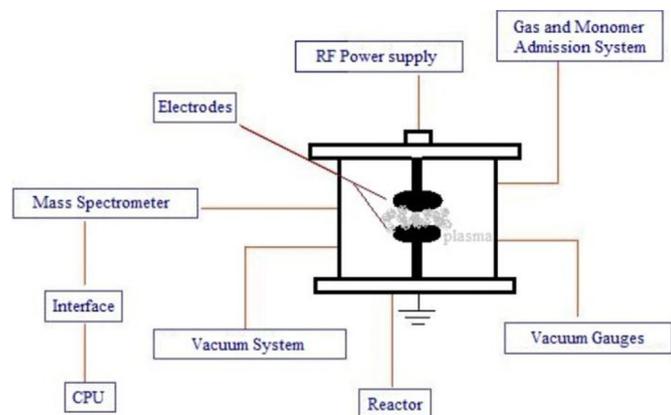


Fig. 1. Block diagram of the experimental setup.

Table 1

Main ionized fragmented species from diglyme/argon plasma.

Ionic fragments and gas	Chemical structure	Mass/charge ratio (m/z)
1	H ⁺	1
2	H ₂ ⁺	2
3	CH ₃ ⁺	15
4	CH ₂ CH ₂ ⁺	28
5	CHO ⁺	29
6	CH ₃ O ⁺	31
7	CH ₂ CH ₂ O ⁺ or CH ₂ OCH ₂ ⁺	44
8	CH ₃ OCH ₂ ⁺	45
9	CH ₃ OCH ₂ CH ₂ ⁺	59
argon	Ar ⁺	40

2. Experimental setup

The glow discharges were generated by an RF power supply operating in the range of 1–40 W, in diglyme/argon atmospheres ranging from 1 to 30 Pa within a cylindrical stainless steel plasma

reactor with 210 mm of internal diameter and 225 mm long. The chamber is provided with eight lateral entrances, positioned at mid plane between the electrodes, that may be used for setting optical, electrical and mass diagnostics and low (mechanical pump) and high (turbo-molecular pump) vacuum systems. The vacuum inside the plasma chamber is monitored by PiraniTM (thermocouple) and PenningTM (inverse magnetron) gauges. A turbo-molecular pump is coupled to the chamber through a gate valve, which is used for cleaning. The pressure is pumped down to 10⁻⁴ Pa, being the chamber purged with argon several times before each experimental run. Diglyme as a liquid monomer was placed inside a stainless steel bottle and it was fed into the plasma chamber through a needle valve. In order to evaporate the monomer and avoid its condensation, the bottle and the plasma chamber were heated thermally at 50 Celsius degrees. The plasma was excited by an RF power supply operating at 13.56 MHz which output intensity may vary from 0 to 300 W (Tokyo HY-Power model RF-300TM). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300TM) that allows one to minimize the reflected RF power. The plasma chamber has two circular parallel plate electrodes measuring 100 mm diameter each one. The upper electrode is coupled to power supply and the other one, which is grounded, contains 20 × 10 mm aluminum substrates. The substrates were previously cleaned using acetone and isopropyl alcohol at ultrasonic apparatus. The mass spectrometry was conducted using a quadrupole mass spectrometer that contains a cylindrical energy analyzer with 45° trajectory curve (Hiden Analytical model EQP-300TM). It operates in a mass range from 1 to 140 a.m.u. for 2.9 eV reference of energy filter. The spectrometer mass resolution is 1 count per second in ionic signal detector [30]. The block diagram of the experimental setup is presented in Fig. 1.

Plasma polymerized films from diglyme/argon were deposited on aluminum substrates during 30 min for all power and pressure conditions. FTIR spectra were obtained using a Perkin Elmer spectrometer model Spectrum 100TM.

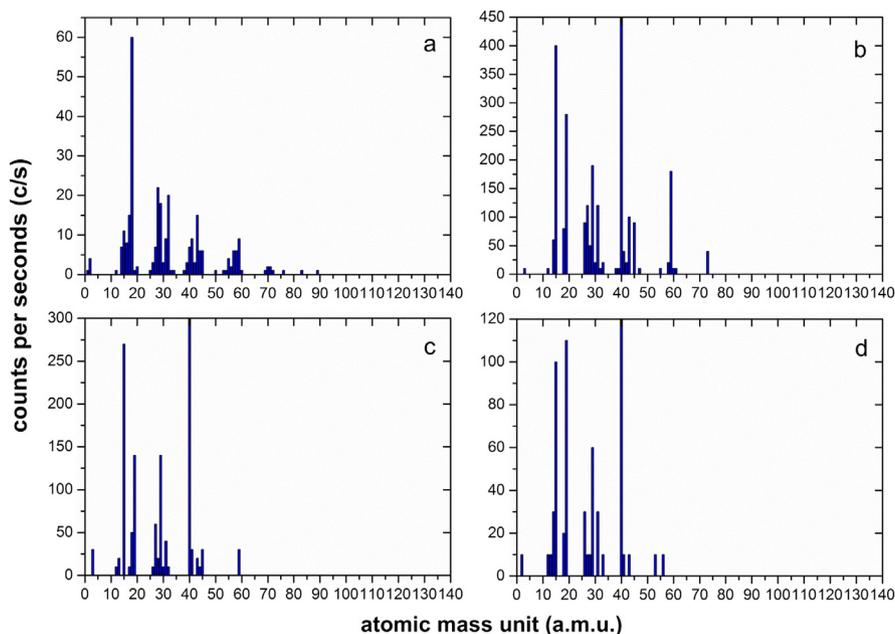


Fig. 2. a: background spectrum for residual species (from gases and/or monomers) into the plasma chamber, evacuated till 0.1 Pa (mass spectrometer operating in RGA mode). b, c and d: mass spectra of diglyme/argon discharges at 15 W for 13.3 Pa diglyme/2.7 Pa argon (16.0 Pa total pressure), 13.3 Pa diglyme/5.3 Pa argon (18.6 Pa total pressure) and 13.3 Pa diglyme/8.0 Pa argon (21.3 Pa total pressure), respectively, with spectrometer operating in ion analysis mode (+IonsIMS).

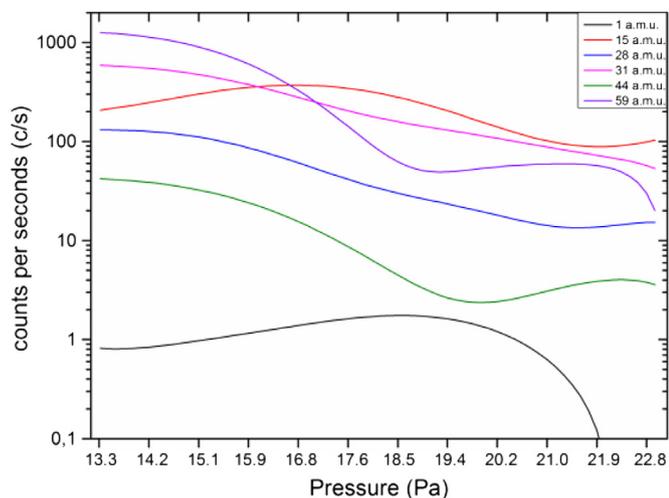


Fig. 3. Pressure dependence of different species from diglyme at 15 W. Started at 13.3 Pa of diglyme, the discharge pressure is increased with argon introduction in the plasma chamber. The signal was smoothed.

3. Results and discussions

Table 1 shows the main ionized fragments that are present in diglyme/argon plasma discharges. They can come from primary fragmentations as CH_3^+ , CH_3O^+ , $\text{CH}_3\text{OCH}_2^+$ and $\text{CH}_3\text{OCH}_2\text{CH}_2^+$, secondary or higher order fragmentations as CHO^+ , CH_2CH_2^+ and $\text{CH}_2\text{CH}_2\text{O}^+$, or from recombination, as H_2^+ . Argon ion is also present. By observing the chemical structure of diglyme presented in the introduction, the fragmentation breaks occur at the chemical bonds of carbon–carbon, carbon–oxygen and carbon–hydrogen. Special attention should be given to fragment $m/z = 44$ ($\text{CH}_2\text{CH}_2\text{O}^+$ or $\text{CH}_2\text{OCH}_2^+$), that is responsible for the formation of PEO-like plasma polymer films that may have a non-fouling characteristic [24].

In Fig. 2 are shown: background spectrum for residual species (from gases and/or monomers) into the plasma chamber, evacuated till 0.1 Pa (a) and for different mixtures of diglyme/argon to 15 W of power (b, c and d). As can be seen in a, after the chamber has been evacuated by the turbo molecular pump and the argon plasma is

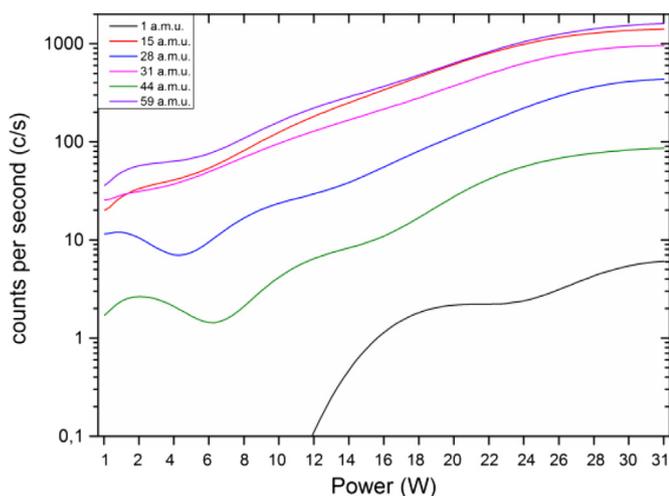


Fig. 4. RF power dependence of different species from diglyme in a discharge of diglyme/argon at 10.0 Pa diglyme/3.3 Pa argon (13.3 Pa total pressure). The signal was smoothed.

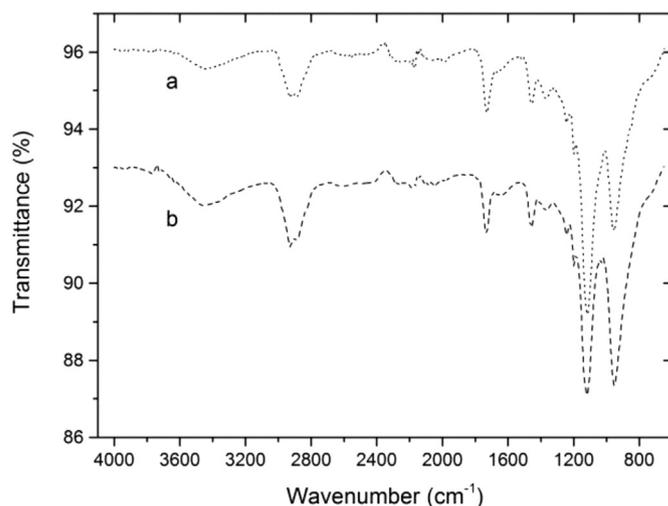


Fig. 5. Infrared spectra of thin films from diglyme plasmas at 5 W (b) and 15 W (a) and 13.3 Pa diglyme/0.0 Pa argon (13.3 Pa total pressure).

set, water (18 a.m.u.), nitrogen (28 a.m.u.), oxygen (32 a.m.u.) and other impurities are still present within the system. In order to obtain the background, it is necessary to use a high electron energy source capable of ionizing the neutral species within the spectrometer. Many of these species are found over the inner walls of the spectrometer, thus, only oxygen, nitrogen and water molecules are considered from the reactor chamber. However, this spectrum presents low ionic signal count rates. The electron source was only used to obtain the background (where no discharge is performed), and all the other results of mass spectrometry related to ionized species from the plasma medium. As it can be observed in b, c and d, (13.3 Pa diglyme/2.7 Pa argon, 13.3 Pa diglyme/5.3 Pa argon and 13.3 Pa diglyme/8.0 Pa argon, respectively) all species presented in Table 1 are present in the spectra. When argon increases inside the reactor, all species tend to have a reduction in the ionic signal count rate which is due to the fact that with an increase of the total pressure, the mean free path decreases in the plasma, thus the electrons present in the plasma lose part of their energy in inelastic collisions altering the energy distribution function, and thus decreasing the ionization processes. Another process that can

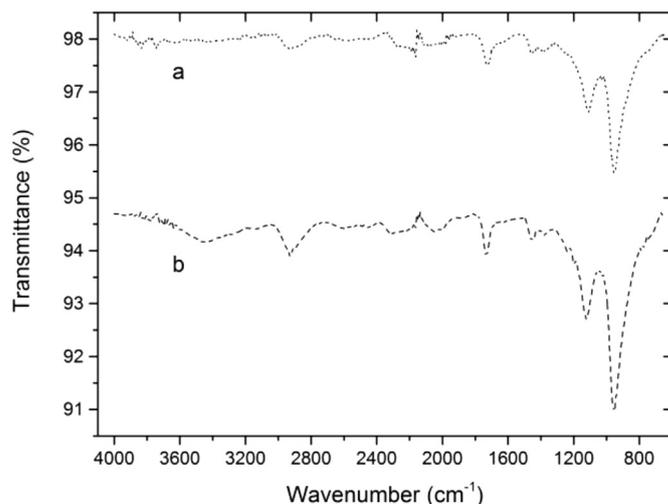


Fig. 6. Infrared spectra of thin films from diglyme/argon plasmas at 5 W (b) and 15 W (a) and 9.4 Pa diglyme/3.9 Pa argon (13.3 Pa total pressure).

Table 2
Integrated absorption (in arbitrary units) of the chemical bonds present in the thin films showed in FTIR spectra.

Bond, wavenumber (cm ⁻¹)		Integrated absorption (a.u.)			
		5 W diglyme/argon	15 W diglyme/argon	5 W diglyme	15 W diglyme
O–H	(3600–3200)	47.5	17.8	36.1	47.8
C–H	(3000–2800)	28.2	17.5	69.7	52.4
C=C	(1800–1750)	15.6	17.6	40.1	31.5
C–H	(1480–1350)	2.2	8.0	11.1	16.6
C–O–C/C–O	(1200–1000)	78.0	58.7	247.5	291.2

induce this behavior is the charge transfer occurring between collisions of argon atoms with ionized species, so changed to neutral species. It is important to note that the proportions between different species vary as shown in Fig. 3.

Fig. 4 shows the evolution of species as function of the plasma applied power at a total pressure of 13.3 Pa (10.0 Pa diglyme/3.3 Pa argon). It is observed that, when the plasma power increases, CH₃+ and CH₃O+ species start reaching great proportions in the plasma. The increase of these species disfavors the deposition of polymeric thin films with more organized structures, as PEO-like ones.

The CH₃OCH₂CH₂+ (59 a.m.u.) species most often have high counts because one molecule of the monomer can generate two of those species through primary fragmentations.

An important characteristic of the presently studied diglyme/argon plasmas just in relation to diglyme discharges, as presented by Algatti MA et al. [31], with similar conditions of pressure and applied power, is that the proportions between the species change significantly in the diglyme/argon mixture.

In Figs. 5 and 6 are shown the corresponding infrared spectra of thin films deposited by plasma from diglyme (a: 5 W, b: 15 W) and diglyme/argon mixture (a: 5 W, b: 15 W). In all spectra shown in these figures the same types of chemical bonds or functional groups are present in the films. The absorptions between 3600 and 3200 cm⁻¹ correspond to hydroxyl (O–H) group and absorptions between 1800 and 1700 cm⁻¹ correspond to C=C vibrations. These types of bonds, O–H and C=C, are not present in molecular structure of the diglyme monomer, so they are formed from chemical recombination that can occur in plasma, in plasma/surface interaction or when the film is exposed to atmospheric air in the particular case of O–H bond. It occurs in accordance of activated growth mechanisms proposed by d'Agostino [13] and Yasuda [10]. Between 3000 and 2800 cm⁻¹ were observed C–H stretching vibrations in CH₂ and CH₃ groups and C–H bending vibrations in CH₂ and CH₃ groups near 1420 and 1350 cm⁻¹. Absorption bands in these spectra between 1200 and 1000 cm⁻¹ are due to C–O and C–O–C coexisting groups.

FTIR spectroscopy is a useful qualitative technique, but it may present semi-quantitative results when comparing particularly bands of the same type. Calculations according to the methods described by Rand, Lamford [32] describe how to find approximate values for the quantification corresponding to each chemical bond into the absorption band. This method is known as integrated

Table 3
Ionic signal count rates for 15 W applied power in discharges of diglyme/argon mixture and diglyme.

Ionized species (m/z)	Ionic signal counting (c/s)	
	15 W diglyme/argon	15 W diglyme
CH ₃ +	(15) 292	207
CH ₂ CH ₂ +	(28) 47	131
CH ₃ O+	(31) 192	581
CH ₂ CH ₂ O+ or CH ₂ OCH ₂ +	(44) 9	42
CH ₃ OCH ₂ CH ₂ +	(59) 328	1247

absorption. In the present work it was applied to the bands between 3600 and 3200 cm⁻¹ (O–H); 3000–2800 cm⁻¹ (C–H stretching); 1800–1700 cm⁻¹ (C=C); 1420–1350 cm⁻¹ (C–H bending); 1200–1000 cm⁻¹ (C–O–C and C–O). The results can be seen in Table 2. The films deposited at 5 W by diglyme/argon plasma measured 90 nm and 95 nm thickness at 5 W and 15 W respectively. On the other hand, the films deposited by diglyme plasmas at 5 W and 15 W presented 140 nm and 210 nm thickness respectively. Therefore, in each condition of deposition, which is governed by plasma parameters, it was obtained thin films containing different molecular structures but presenting the same types of chemical bonds.

From the results shown in Table 2, corresponding to the integrated absorption of the films, a qualitative parallel can be made with the results obtained from the mass spectrometry of plasma phase. Table 3 shows the ionic signal counts for the ratios m/z 15 (corresponding to CH₃+); 28 (CH₂CH₂+); 31 (CH₃O+); 44 (CH₂CH₂O+ or CH₂OCH₂+); 59 (CH₃OCH₂CH₂+), taken as reference 15 W discharges of diglyme/argon mixture and diglyme respectively. It is noticed an increase for the ratios m/z 31, 44 and 59, which correspond to the species that contain C–O and C–C–O and/or C–O–C bonds, in plasma from diglyme when compared to plasma from diglyme/argon. Moreover, C–O–C and C–O chemical bonds are also in more quantities in the films deposited from plasma diglyme. Thus, increasing relative amounts of species in the plasma phase presenting m/z 31, 44 and 59 ratios the chemical bonds between polymeric structures containing C–O–C and C–O in the thin films are favored.

A thin film shows the PEO-like character when its polymeric structure tends to repeat (CH₂CH₂O)_x, forming successive chains [24]. In this work it tends to occur more easily for films deposited by diglyme plasma.

4. Conclusions

The ionic signal count rates decreases with argon introduction in diglyme discharges due to the increasing in operating pressure and charge transfer, thus, it changes the composition of ionic species in plasma phase.

The FTIR analysis showed that all films produced exhibit the same bonds in their molecular structures. However, by the integrated absorption calculus it could be observed that the structures differ for each discharge condition.

The presence of argon in the diglyme/argon mixture did not show advantage to increase the thickness of thin films and did not contribute to increase the amount of species presenting m/z = 31, 44 and 59 in the discharge in comparison with diglyme plasmas.

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