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Wettability, optical properties and molecular structure of plasma polymerized diethylene glycol dimethyl ether

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Abstract. Modern industry has frequently employed ethylene glycol ethers as monomers in plasma polymerization process to produce different types of coatings. In this work we used a stainless steel plasma reactor to grow thin polymeric films from low pressure RF excited plasma of diethylene glycol dimethyl ether. Plasmas were generated at 5W RF power in the range of 16 Pa to 60 Pa. The molecular structure of plasma polymerized films and their optical properties were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy, respectively. The IR spectra show C-H stretching at 3000-2900 cm⁻¹, C=O stretching at 1730-1650 cm⁻¹, C-H bending at 1440-1380 cm⁻¹, C-O and C-O-C stretching at 1200-1000 cm⁻¹. The refraction index was around 1.5 and the optical gap calculated from absorption coefficient presented value near 3.8 eV. Water contact angle of the films ranged from 40° to 35° with corresponding surface energy from 66 to 73×10⁻⁷ J. Because of its favorable optical and hydrophilic characteristics these films can be used in ophthalmic industries as glass lenses coatings.

1. Introduction

Material processing using low-temperature low-pressure RF excited plasmas is essential in many current scientific and technological issues encompassing microelectronics, optical and biomaterial industries [1-13]. The main reason is that within such kind of plasmas electrons may attain energy in excess of several eV in comparison with the heavy particles present in the discharge. This unusual thermal non-equilibrium situation is very efficient in molecular fragmentation through electron impact. This feature of such plasmas gives rise to a very reactive chemistry in a relative cold environment whose kinetics is not easily controlled [1-9]. Therefore it is essential to perform different plasma diagnostics in order to probe the trends of chemical species as well as the electrons behavior for different plasma parameters, such as RF power coupled to the plasma chamber, gas pressure, gas flow and so on [2,3,7].

In the field of biomaterial science and technology, plasma polymerized polyethylene glycol dimethyl ether has been attracting the attention of the scientific community due to its non-fouling properties [14-19]. If appropriate plasma parameters are set, polymer films can be synthesized keeping

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quite similar molecular structure to that of polyethylene oxide-like (PEO-like) with the advantage that these films are not soluble in water. The aqueous solubility of PEO makes it inappropriate for many biomaterial 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: film deposition under low mean RF power level by controlling the power supply on/off ratio [19,20], decreasing of monomer residence time and consequently the reduction of its interaction with the plasma environment [20], cooling of substrate with liquid nitrogen [21], energy reduction of the ions reaching the substratum [4], and so on.

In order to determine the appropriate experimental parameters that would result in customized hydrophilic transparent film in plasma polymerization of PEO-like coatings this paper deals with plasma polymerization of diglyme at relatively low RF power levels using silicon and quartz plates as substrates. Molecular structure, optical properties and the hydrophilic/hydrophobic characteristics of plasma polymerized diglyme at 5 W of RF power and for different values of pressure within plasma chamber, were characterized using FTIR, ultraviolet spectroscopy, and contact angle measurements respectively. The optical characteristics of plasma polymerized diglyme were obtained by measurements of refraction index, absorption coefficient and optical gap

2. Experimental setup

Diglyme ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$) plasmas were excited by a RF power supply operating in 13.56 MHz whose output power could be adjusted 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 minimizing the reflected RF power. All experiments were run with the RF output kept fixed on 5 W in diglyme atmospheres in the pressure range from 16 Pa (120 mTorr) to 60 Pa (450 mTorr) within a stainless steel cylindrical, 210 mm of internal diameter and 225 mm long, parallel plate electrodes plasma reactor. This reactor is provided with eight lateral entrances, positioned at the mid plane between the electrodes, which can 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 piraniTM (thermocouple) and penningTM (inverse magnetron) gauges. The turbo-molecular pump is connected to the chamber through a gate valve and is used for cleaning purposes. The pressure is pumped down to 1.33×10^{-4} Pa (10^{-6} Torr), and the chamber is purged with argon several times before each 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 from a stainless steel bottle was fed into the plasma chamber through a needle valve. The mass spectrometry was realized using a mass spectrometer and energy analyzer (Hiden Analytical model EQP-300TM), operating in the mass and energy range from 1 to 300 amu and from 0 to 100 eV, respectively. The background mass spectra with the plasma turned off were carried out at the same pressure conditions of each diglyme plasma polymerization processes. These spectra were used to control the number of chemical species resulting from the fragmentation within the mass spectrometer and also to detect the presence of contaminants resulting from the plasma chamber cleaning process. The block diagram and the photograph of the experimental setup are presented in figures 1 and 2, respectively.

Diglyme films were deposited on silicon and quartz substrates for one hour for all pressure conditions. Film thickness was determined through step meter technique using an Alpha Step Tencor-100TM. Typical polymer film thickness varied from 100 nm to 140 nm. Diglyme films for IR and ultraviolet-visible (UV-Vis herein) analysis were deposited on glass plates previously covered with aluminium films and quartz plates, respectively. FTIR and UV-Vis spectra were obtained using Jasco FTIR-100TM and Perkin Elmer Lambda-9TM spectrometers, respectively. The hydrophobic/hydrophilic characteristics of plasma-polymerized Diglyme were investigated through contact-angle measurements using water as probe liquid and the Ramé-Hart goniometer model 100TM.

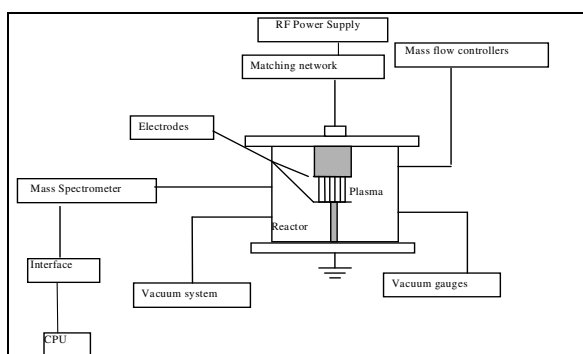


Figure 1. Block diagram of the experimental setup used in plasma polymerization of diglyme films.

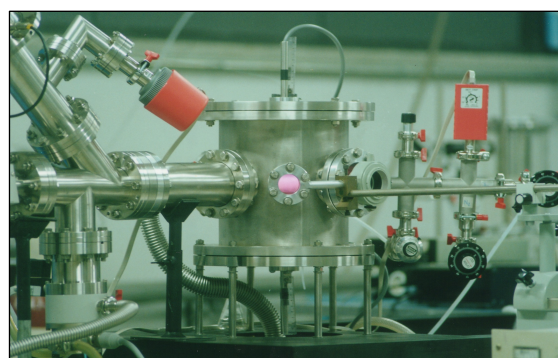


Figure 2. Photograph of the experimental arrangement.

3. Results and Discussion

Figure 3 shows typical infrared spectra of diglyme plasma polymers. The absorption bands at 2960 cm^{-1} and 2900 cm^{-1} are associated to C-H stretching modes in CH_3 and CH_2 groups, respectively. The absorption band between 1730 cm^{-1} and 1650 cm^{-1} is due to C=O stretching. The absorptions observed in the wavenumber range from 1440 cm^{-1} to 1380 cm^{-1} are due to C-H bending modes. The strong band in the range from 1200 cm^{-1} to 1000 cm^{-1} is associated with C-O and C-O-C stretching modes. The IR spectra of plasma polymerized diglyme films demonstrate the preservation of some functional groups of diglyme monomer's structure, i.e. $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$. The absorption peak due to O-H stretching near $3500\text{--}3200\text{ cm}^{-1}$ indicates the presence of the polar radical OH incorporated into the polymer structure at the pressure of 59 Pa (440 mTorr). This behavior may be understood if one takes into account the spectrum of the monomer Diglyme shown in figure 4. It can be seen a strong absorption peak due to O-H stretching from the water molecules incorporated to the monomer.

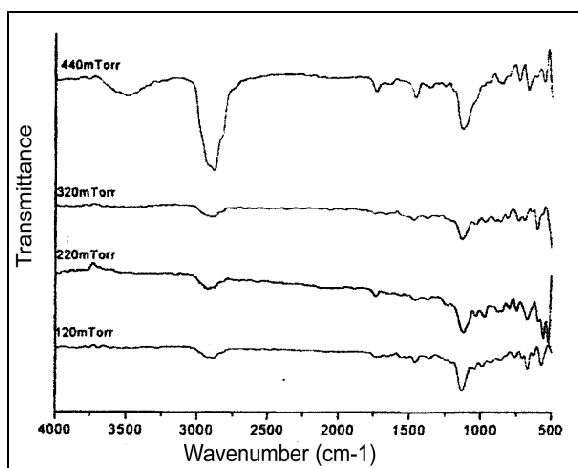


Figure 3. Infrared spectra of plasma polymerized diglyme films for different values of gas pressure.

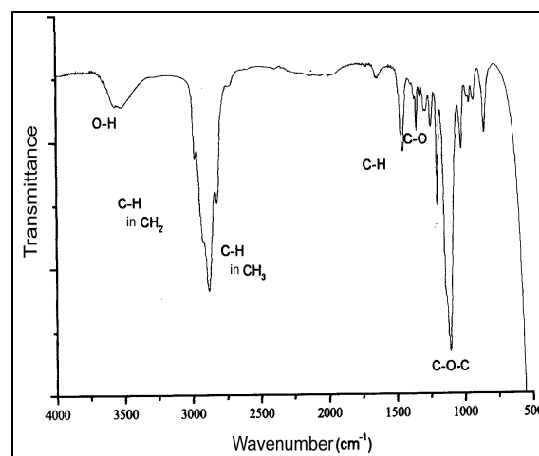


Figure 4. Infrared spectra of diglyme monomer.

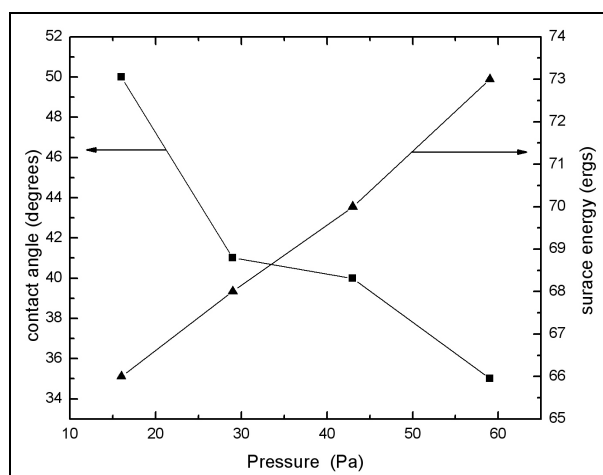


Figure 5. Contact angle and Surface energy versus pressure for plasma polymerized diglyme films.

The comparison between IR spectra in figures 3 and 4 allows us to conclude that for RF power kept fixed on 5 W plasma discharges were favorable for the retention of main monomer's functional groups on plasma polymerized Diglyme films. These results show that the PEO-like characteristics of Diglyme films were preserved for the pressure range investigated in the experiment.

The results presented in figure 5 show that the water contact angle decreases monotonically with the increasing of pressure with the corresponding increasing of surface energy. This is in close agreement with the IR spectra that show the incorporation of O-H radical into the plasma polymerized diglyme film with the increasing of pressure. It also should be stressed that the increasing of pressure enhances the PEO-like characteristics of the films due the reduction of the electron mean free path within the discharge which favors the electronic elastic scattering [2,3].

The refractive index and the optical-absorption coefficient have been determined for plasma polymerized diglyme films deposited at different values of gas pressure. The calculations were performed from the data of the UV-Vis transmission spectra using the procedure outlined in [22,23]. The refractive index of about 1.5, calculated for photon energy of 2.0 eV, remained approximately constant for plasma polymerized diglyme films deposited at different values of gas pressure inside the plasma chamber. These results show that these films may be used as anti-reflecting protective coatings in ophthalmic industries. The optical gap of the plasma polymerized Diglyme films at a fixed relative low value of RF power (5 W) for pressure ranging from 16 Pa to 60 Pa remained approximately constant around 3.8 eV.

4. Conclusions

Plasma polymerized diglyme films deposited at 5 W RF power and monomer pressure varying from 16 Pa (120 mTorr) to 60 Pa (450 mTorr) are transparent to visible light and therefore can be used in ophthalmic industries as protective anti-reflecting coatings. The IR analysis of polymeric films revealed that the operation of the plasma chamber at relative low RF power level was successful in producing plasma polymerized diglyme whose structure resembles the monomer's one. The increasing of the gas pressure inside the plasma chamber favours the fragmentation of the monomer by electron impact and the recombination processes keeping many monomers' functional groups on the polymeric films structure. These deposition conditions enhanced the PEO-like characteristics of plasma polymerized diglyme films keeping the refractive index and the optical gap approximately constant around 3.8 eV. Therefore one can conclude that the careful setup of plasma diagnostics such as mass spectrometry and optical spectroscopy result in thin plasma polymerized diglyme films with customized optical properties.

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References

- [1] d'Agostino R, Favia P, Oehr C and Wertheimer M R 2005 Low-temperature plasma processing of materials: past, present and future *Plasma Process. Polym.* **2** 7-15
- [2] d'Agostino R, Favia P, Kawai Y, Ikegami H, Sato N and Arefi-Konsari F 2008 (eds) *Advanced Plasma Technology* (Weinheim, Germany: Wiley-VCH)
- [3] Hippler R, Kersten H, Schmidt M and Shoenbach K H 2008 (eds) *Low Temperature Plasmas: Fundamentals, Technologies and Techniques* (Weinheim, Germany: Wiley-VCH)
- [4] Biederman H 2004 (ed) *Plasma Polymer Films* (London: Imperial College Press)
- [5] Bogaerts A, Neyts E, Gijbels R, van der Mullen J 2002 *Spectrochim. Acta B* **57**, 609
- [6] Chu P K, Chen J Y, Wang L P, Huang N 2002 *Mat. Sci. Eng. Rep.* **36**, 143-206
- [7] Shul R J, Pearton S J 2000 (eds.) *Handbook of Advanced Plasma Processing Techniques*, (Springer, Berlin)
- [8] Inagaki N 1996 *Plasma Surface Modification and Plasma Polymerization*, (Technomic Publishing Company, Inc., USA)
- [9] Yasuda H 1985 *Plasma Polymerization*, (New York: Academic Press, Inc., USA)
- [10] Roth J R 1995 *Industrial Plasma Engineering: Principles*, v. 1, (UK: IOP Publishing)
- [11] Roth J R 2001 *Industrial Plasma Engineering: Applications*, v. 2, (UK: IOP Publishing)
- [12] d'Agostino R 1990 (ed.) *Plasma Deposition, Treatment and Etching of Polymers*, (New York: Academic Press)
- [13] d'Agostino R, Favia P, Fracassi F 1997 (eds.) *Plasma Processing of Polymers, NATO ASI series E: Applied Sciences vol. 346*, (Dordrecht, The Netherlands: Kluwer Academic Publishers)
- [14] Alcantar N A, Aydil E S, Israelachvili J N 2000 *J. Biomed. Mat. Res.* **51**, 343
- [15] Favia P, d'Agostino R 1998 *Surf. Coat. Technol.* **98**, 1102
- [16] Hendricks S K, Kwok K, Shen M, Horbett T A, Ratner B D, Bryers J D 2000 *J. Biomed. Mat. Res.* **50**, 160
- [17] Sardella E, Gristina R, Senesi G S, d'Agostino R and Favia P 2004 Homogeneous and micropatterned plasma-deposited PEO-like coatings for biomedical surfaces *Plasma Process. Polym.* **1** 63-72
- [18] Sardella E, Favia P, Gristina R, Nardulli M and d'Agostino R 2006 Plasma-aided micro- and nanopatterning processes for biomedical applications *Plasma Process. Polym.* **3** 456-69
- [19] Cicala G, Creatore M, Favia P, Lamendola R, d'Agostino R 1999 *Appl. Phys. Lett.* **75**, 37
- [20] Oehr C, Müller M, Elkin B, Hegemann D, Vohrer U 1999 *Surf. Coat. Technol.* **116-119**, 25
- [21] Biederman H, Slavínská D 2000 *Surf. Coat. Technol.* **125**, 371
- [22] Durrant E, Mota R P, Moraes M B 1992 *J. Appl. Phys.* **71**, 448
- [23] Cisneros J L, Rego G B, Tomyiama M, Bilac S, Gonçalves J M, Rodriguez A E, Argüello Z P 1983 *Thin Solid Films* **100**, 155