Romanian Reports in Physics **70**, 507 (2018)

THICKNESS DEPENDENT AC CONDUCTIVITY OF PLASMA POLY (ETHYLENE OXIDE) THIN FILMS

KEMAL ULUTAS

Istanbul University, Science Faculty, Physics Department,
Vezneciler, Istanbul, 34459, Turkey
E-mail: hku@istanbul.edu.tr

Received October 12, 2017

Abstract. The properties of thin film polymers such as low dielectric constant, high thermal and photo balance, high chemical resistance and high optical transmittance are widely used in optic and microelectronics. In this work, plasma poly(ethylene oxide) (pPEO) thin films in different thicknesses were deposited between Aluminum (Al) electrodes on glass substrates by plasma assisted physical vapor deposition (PAPVD) technique at Argon plasma under 10^{-3} Torr. The plasma was produced at 5 W by magnetron connected to RF power supply. The ac measurements of the samples were made were in the frequency range 10^{-1} Hz -10^{7} Hz and in temperatures from 193 to 353 K with increments of 10 K. Thickness dependent AC conductivity of pPEO thin films can be interpreted by empirical relation $\sigma(\omega)$ α ω^n where ω is the angular frequency and *n* is the parameter. Frequency, temperature and thickness dependence of AC conductivity showed that there were oligomers and free radicals with different sizes produced by plasma polymerization of PEO. The thickness dependence of AC conductivity of plasma PEO samples can be evaluated to adjust AC conductivity and also to adjust the DC-like conductivity which is a results of drift of free charge carriers or the orientation polarization of long oligomers. Three different relaxation mechanisms depending on the film thickness were observed. The effect of the dead layer in the polarization region of long oligomers was determined.

Key words: AC conductivity, thin film, plasma poly (ethylene oxide).

1. INTRODUCTION

In the a few last decades, polymers have attracted much attention in the solution of industrial problems in nanotechnology and electronic devices. Many researchers also work on polymer techniques for the preparation and application of polymer thin films. Recently, polymer thin films play an increasingly important role in technological applications such as coatings, adhesives and lithography on light emitting organic diodes and organic material based devices, including sensors and detectors [1–6].

Plasma-assisted vacuum evaporated polyethylene oxide (PEO), is used in biomedical applications due to its biologic non-fouling properties [7–10]. It also has applications in controlled drug distribution, packaging and optical Technologies [8–10]. Physical properties of polymer films often differ substantially from bulk behavior. For this reason, it is important to examine the properties of the polymers depending on the film thickness.

In the study, plasma poly (ethylene oxide) (pPEO) thin films in different thicknesses were deposited by plasma assisted physical vapor deposition (PAPVD) technique at Argon plasma under 10^{-3} Torr. The variation of AC conductivity of pPEO thin films deposited by plasma assisted physical vapor deposition (PAPVD) technique were given as a function of film thicknesses. The AC measurements of the samples were made in the frequency range 10^{-1} Hz –10^{7} Hz and in temperatures from 193 to 353 K with increments of 10 K.

In the literature, structural and dielectric properties of PEO and pPEO were studied, respectively [11–13]. However, there is no study on AC conductivity of pPEO dependent film thicknesses. We will contribute to the literature by examining the effect of film thicknesses on alternative conductivity.

2. EXPERIMENTAL

Plasma poly(ethylene oxide) (pPEO) thin films were deposited by plasma assisted physical vapor deposition (PAPVD) technique at Argon plasma under 10^{-3} Torr vacuum precisely how this was done is described in the literature [14]. The plasma was produced at 5 W by magnetron connected to RF power supply. Thickness of the Plasma poly (ethylene oxide) (pPEO) thin films was 20 nm, 100 nm, 250 nm, 500 nm. An ellipsometry system (Woollam M-2000 DI) was to determine thickness of the plasma PEO samples. Our samples have an Al/Plasma poly (ethylene oxide) (pPEO) thin film/Al configuration on the glass substrates. The capacitance (C) and dissipation factor (tanδ) of the samples were measured using a Hewlett Packard impedance analyzer (4192 A) in the frequency range 10^{-1} Hz –10^{7} Hz and in temperatures ranging from 193 to 353 K with increments of 10 K. A copper-constantan thermocouple was used to determine the temperatures of the samples. The dielectric constant ε_1 of the samples can be calculated by measuring the capacitance (C); thickness (d), free space permittivity (ε_0) and area of the dielectric layer (A) and using the capacitance formula $\varepsilon_1 = Cd/\varepsilon_0 A$.

Ac conductivity (σ_{ac}) has been evaluated from the dielectric data in accordance with the relation $\sigma_{ac} = \omega\varepsilon_0\varepsilon_r \tan\delta$, where $\varepsilon_r = C / C_0$ is the relative permittivity, tanδ is the tangent loss factor, C_0 is the vacuum capacitance of the cell.

3. RESULTS AND DISCUSSION

Frequency and temperature dependent AC conductivity shows that there are three relaxation mechanism in the investigated frequency and temperature range for all thicknesses as seen in Figs. 1–4. The AC conductivity obeys equation (1),

$$\sigma_{AC} = A\omega^n, \tag{1}$$

where, A is a coefficient, ω is angular frequency and n is an integer [15–20]. To distinguish the relaxation mechanisms fitted lines are shown with different colors. The relaxation mechanism which expand in all frequencies range at high temperatures is referred with black line. The relaxation mechanism which expands in all frequency range at mid temperatures is referred with red line. Besides, the relaxation mechanism observed at low temperatures is shown with blue line. The fit lines shift toward lower frequencies with decreasing temperature. The mechanism described by black line is observed at low frequencies. This mechanism can be attributed to polarization of large oligomers (-CH2-CH2-O- and derivatives) which appear following the fragmentation of long PEO backbone as a result of plasma polymerization [7]. These oligomers are the biggest components of plasma PEO network. In order to polarize the biggest charge carriers it is needed to apply the highest temperature and lowest frequency. As shown in Fig.1, high temperature relaxation mechanism can be observed only at the highest temperature.

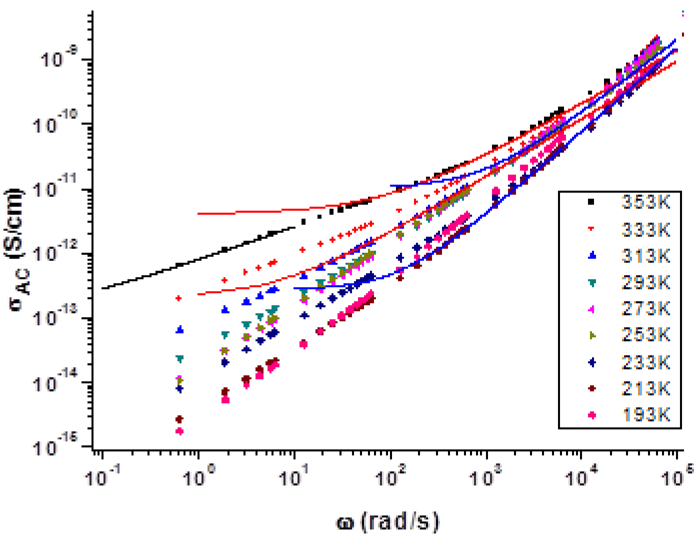

Fig. 1 – (Color online) Frequency dependence of AC conductivity for 20 nm.

When the frequency dependence of AC conductivity for 100 nm Plasma PEO sample is investigated, it is observed that the high temperature polarization mechanism with black fitting lines of 100 nm sample can be detected at higher frequencies than of 20 nm sample as shown in Fig. 2.

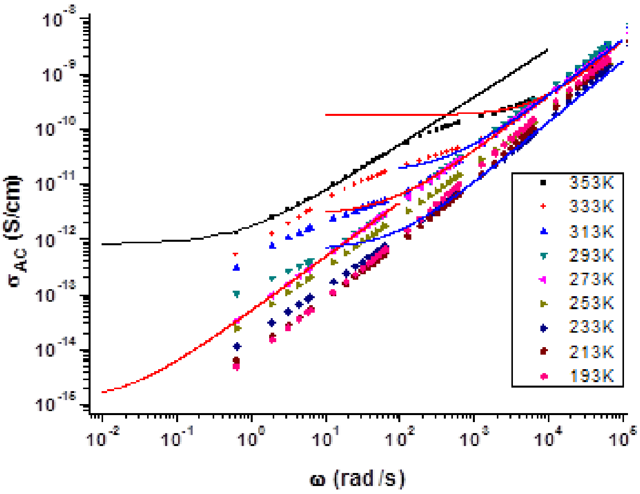

Fig. 2 – Frequency dependence of AC conductivity for 100 nm.

For 250 and 500 nm plasma PEO samples the polarization mechanisms described by black fitting lines can be observed at lower temperatures than of 20 and 100 nm plasma PEO samples as shown in Figs. 3 and 4.

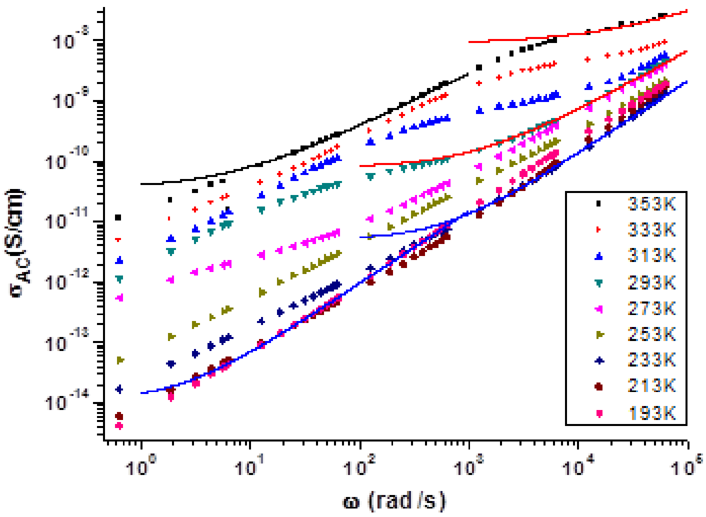

Fig. 3 – Frequency dependence of AC conductivity for 250 nm.

Black fitting lines referres to polarization of long oligomers as mentioned before [21–24]. As a result of behaviors of AC conductivity for this polarization mechanism can be connected to increasing free space to be polarized and the effect of dead layer which is a result of good adhesion of plasma polymer layers to any substrates [25–28].

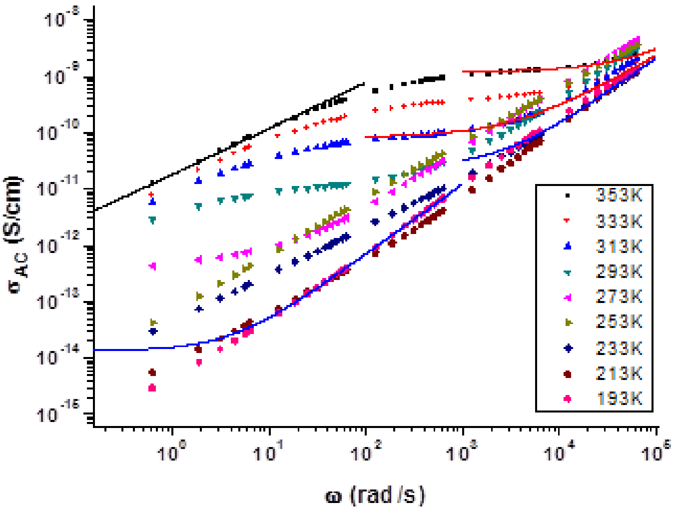

Fig. 4 – Frequency dependence of AC conductivity for 500 nm.

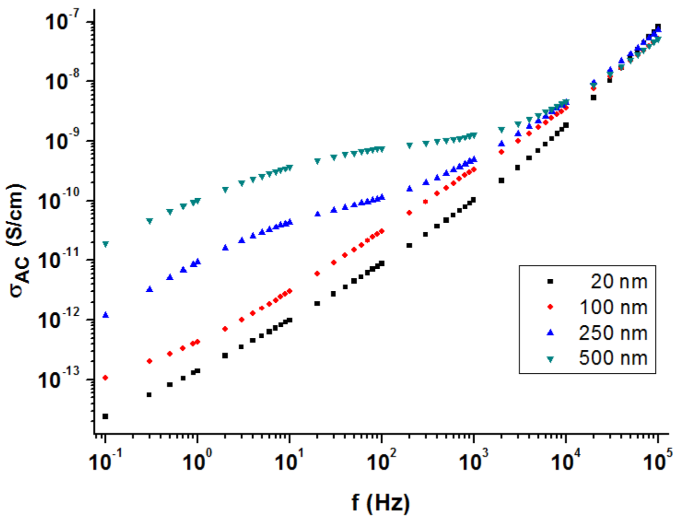

Fig. 5 – Frequency and thickness dependence of AC conductivity at room temperature.

Other polarization mechanisms described by red and blue line can be attributed to polarization of small oligomers and free radicals, the products of plasma polymerization [7]. These polarization mechanisms shift toward lower frequencies with decreasing temperature as observed for the polarization the mechanism with black fitting lines.

At room temperature AC conductivity exhibits a behavior depending on thickness in the investigated frequency interval as shown in Fig. 5. Similar comparison can be applied for other temperatures. It is observed that particularly at low frequency side of the frequency range there is a pronounced increase of AC conductivity with increasing thickness. Probably, at this temperature for example at 1 Hz for 250 and 500 nm samples the dominant mechanism is the polarization of long oligomers described by black lines while at the same frequency for 20 nm and 100 nm samples the dominant mechanism is the polarization of short oligomers described by red lines. These results show that by lowering the thickness, the polarization of long oligomers can be controlled. Also the AC conductivity can be decreased by decreasing thickness. Here the main effect can be expressed as dead layer [25–29].

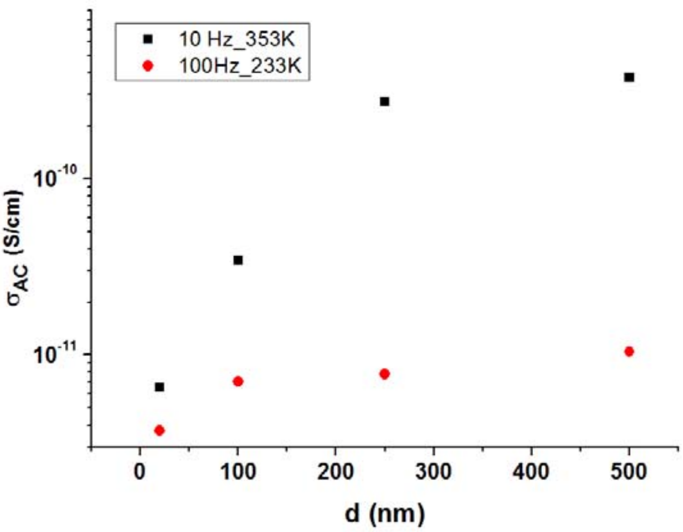

Fig. 6 – Thickness dependence of AC conductivity at certain frequencies and certain temperatures.

To realize the difference between the effects of mechanisms observed at high temperatures-low frequencies and low temperatures-high frequencies, the graph in Fig. 6 can be investigated. It can be interpret that at low frequencies and high temperatures AC conductivity is mainly affected by polarization of long oligomers (black points) while at high frequencies and low temperatures AC conductivity is affected by small oligomers or radicals [21–24]. Besides, dead layer effect causes about 100 times difference in AC conductivity depending on thickness

4. CONCLUSION

Understanding the effect of film thickness on the dielectric properties of polymers is important to the development of electronic device applications. In this work, plasma PEO thin film samples with different thicknesses were deposited at 5 W plasma discharge power. Frequency, temperature and thickness dependence of AC conductivity showed that there were oligomers and free radicals with different sizes produced by plasma polymerization of PEO. Depending on size three different relaxation mechanisms were observed. The effect of dead layer which was particularly influenced on thinner films was clearly detected at the polarization region of long oligomers. Lowering thickness and the increasing effect of dead layer caused to minimize the free volume for the oligomers to be polarized and the dead layers restricted the orientation of the oligomers. The clear thickness dependence of AC conductivity of plasma PEO samples can be evaluated to adjust AC conductivity and also to adjust the DC-like conductivity which is a results of drift of free charge carriers or the orientation polarization of long oligomers.

These results will contribute to literature by advising to change dielectric and structural properties of plasma PEO thin films by varying the thickness in addition to plasma discharge power.

REFERENCES

1. A. J. Bur, Polymer **26**, 963 (1985).
2. J. J. Aklonis, J. Chem. Education **58**, 892 (1981).
3. D. D. C. Bradley, Chem. Brit. **27**, 719 (1991).
4. A. Burke, J. Power Sources **91**, 37 (2000).
5. T. Le, Y. Kim and H. Yoon, Polymers **9**, 150 (2017).
6. G. Kaur, R. Adhikari, P. Cass, M. Bown and P. Gunatillake, RSC Adv. **5**, 37553 (2015).
7. A. Choukourov, A. Grinevich, O. Polonskyi, J. Hanus, J. Kousal, D. Slavinska, J. Phys. Chem. B **113**, 2984 (2009).
8. A. Choukourov, I. Gordeev, D. Arzhakov, A. Artemenko, J. Kousal, O. Kylián, Polym. **9**, 48 (2012).
9. A. Choukourov, A. Grinevich, O. Polonskyi, J. Hanus, J. Kousal, D. Slavinska, H. Biederman, J. Phys. Chem. B **113**, 2984 (2009).
10. Venkat K. Vendra, Lin Wu, Sitaraman Krishnan, Polymer Thin Films for Biomedical Applications, John Wiley, London, 2011.
11. W. J. Bandar, B. E. Mellander, I. Albinsson, K. L. Dissanayake, J. C. Pitawala, J. Solid State Electrochem. **13**, 1227 (2009).
12. R. J. Sengwa, S. Choudhary, J. Alloys and Comp. **701**, 652 (2017).

13. M. L. Verma, H. D. Sahu, Ionics **23**, 2339 (2017).
14. S. Yakut, H. K. Ulutas, I. Melnichuk, A. Choukourov, H. Biederman, D. Deger, Thin Solid Films **616**, 279 (2016).
15. A. Ghosh, D. Chakravorty, Journal of Physics: Condensed Matter **2**, 5365 (1990).
16. A. Ghosh, Physical Review B **42**, 1388 (1990).
17. A. Ghosh, Physical Review B **42**, 5665 (1990).
18. N. Shukla, A. K. Thakur, A. Shukla, D. T. Marx, Int. J. Electrochem. Sci. **9**, 7644 (2014).
19. R. J. Sengwa, S. Choudhary, Indian Journal of Physics **88**, 461 (2014).
20. S. Choudhary, R. J. Sengwa, Journal of Applied Polymer Science **132**, 41311 (2015).
21. S. Chisca, V.E. Musteata, I. Sava, M. Bruma, European Polymer Journal **47**, 1186 (2011).
22. N. Gondaliya, D. Kanchan, P. Sharma, M. S. Jayswal, Polymer Composites **33**, 2195 (2012).
23. P. Sharma, D. K. Kanchan, Polymer International **63**, 290 (2014).
24. B. K. Money, K. Hariharan, J. Swenson, J. Solid State Ionics **262**, 785 (2014).
25. T. Liang, Y. Makita, S. Kimura, Polymer **42**, 4867 (2001).
26. S. Napolitano, D. Prevosto, M. Lucchesi, P. Pingue, M. D'Acunto, P. Rolla, Langmuir **23**, 2103 (2007).
27. J. L. Keddie, R. A. Jones, R. A. Cory, EPL (Europhysics Letters) **27**, 59 (1994).
28. J. Wang, H. K. Kim, F. G. Shi, B. Zhao, T. G. Nieh, Thin Solid Films **377**, 413 (2000).
29. S. Yakut, K. Ulutas, D. Deger, Thin Solid Films **645**, 269 (2018).