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The thickness dependence of dielectric properties in the plasma polymer thin films

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TURKEY

Abstract:

In this study, the results of dielectric spectroscopy of plasma polymerized poly(ethylene oxide) thin films are presented. The films were deposited by plasma assisted physical vapour deposition at radio-frequency plasma discharge power of 5 W. Thicknesses of the films have 20nm, 100nm, 250nm. Dielectric measurements of the films were performed in the frequency range of 10^{-1} Hz to 10^7 Hz and temperature was scanned between 173 K and 353 K. The dielectric constant (ϵ') and dielectric loss (ϵ'') of plasma polymerized poly(ethylene oxide) thin films were calculated by measuring capacitance (C) and dielectric loss factor ($\tan \delta$).

It was observed that there were two relaxation mechanisms in the investigated frequency range. These were called as α and β relaxations. These relaxations shifts toward higher frequencies with increasing temperature. Besides, α -relaxation starts to appear at different temperatures. This shows the difference between the polarizability abilities of samples at same temperature and same frequencies. The reason of this behavior can be expressed by dead layer concept which is a result of good adhesion of the bottom layer of plasma polymer to the substrate. By the light of these interpretations, with thinner samples it is possible to have structurally similar thin films like thin films deposited at high plasma power. A thinner film may support more transparent and these thinner films may be effective as coverage of optical devices such as lenses, visors etc.

1. Introduction

Thermal, electrical and mechanical properties of polymers are useful for use in technological and biological applications [1–7]. Thin polymer films obtained by plasma polymerization are generally more biocompatible than conventional biomaterials such as Silastic. These films are suitable to change of the surface properties of the substrate without altering its bulk properties. Both the features together indicate the possible biomedical use of plasma polymerization as well as plasma treatment of polymer surfaces processes. Polyethylene oxide (PEO), a member of the polymer family, attracted much attention owing to its non-biodegradable properties. Non-fouling properties were investigated by Choukourov et al. [8]. Non-fouling has many biomedical applications to limit or completely prevent the accumulation of proteins and microorganisms. Plasma poly(ethylene oxide) (pPEO) is used in biomedical applications, controlled drug delivery, packaging technologies and optical applications [9]. Plasma polymer thin films can be obtained at different methods as by changing the deposition pressure, deposition current, monomer flow rate and polymerization. They may have properties such as homogeneity, free from pinholes, water insolubility, high electrical resistance, chemical stability, high cross-linking density, good adhesion and thermal stability [7,10-13]. Plasma polymer thin films, were first deposited by Bradley and Hammes [14]. Furthermore, still it draws attention nowadays. [15–20]. In fact, It can be said that this method opens a new application area in material synthesis. There are various methods to examine the properties of materials such as structural, electrical, optical. Dielectric spectroscopy, one of these methods, is used to investigate the relationship between the structure and molecular dynamics of materials as polymers, plasma polymers and amorphous materials. There are studies in the literature that use dielectric spectroscopy to characterize the plasma polymer. [12,13,21,22]. In addition, there are reports on the dielectric properties of

PEO, pPEO [2, 23,24] and on the comparison of their dielectric properties with the structural properties of plasma polymers [25- 29]. However, there are no reports on of the pPEO dependent on the film thicknesses.

In this work, pPEO thin film samples at different thickness (20 nm, 100nm, 250nm, 500 nm) was analyzed in the frequencies ranging between 10^{-2} Hz– 10^7 Hz and in the temperature ranging between 173 K and 433 K. The dielectric constant (ϵ') and dielectric loss (ϵ'') of Plasma polymer thin films by plasma assisted physical vapour deposition at radio-frequency plasma discharge power of 5 W were calculated by measuring capacitance (C) and dielectric loss factor ($\tan \delta$) . In the given intervals, both the dielectric constant and the dielectric loss of the thin films decrease with increasing frequency, but increase with increasing temperature. This behavior can be explained as multicomponent polarization in the structure.

2.Experimental

Plasma polymer sample deposition was performed using a PAPVD system which was operated in a vacuum chamber with a base pressure of 10^{-3} Pa produced by rotary and diffusion pumps. A copper crucible with 4 cm deep was used for vaporization. One fourth of the crucible was filled with PEO granules (Sigma-Aldrich, Inc., $M_n = 1500$ g/mol) mixed with Cu granules for better heat transfer. The crucible was placed onto parallel molybdenum stripes in order to be heated to 340 °C and radio frequency (RF) magnetron with a graphite target, which was reduced the unwanted contribution of sputtered carbon, was placed 4 cm below the crucible to ignite a glow discharge. The experiments were performed in argon under 1 Pa pressure and 5 cm³ /min flow rate and the discharge power was supplied with an RF generator (Dressler Ceasar-13,56 MHz). The samples were deposited with 5 W discharge power. A Quartz Crystal Microbalance (QCM) was used to adjust the deposition rate to 10

nm/min. The thickness of the pPEO samples was measured by ellipsometry (Woollam M-2000 DI). As the deposition conditions (Ar pressure and flow rate, the discharge power and deposition rate) were stabilized, the substrates were introduced into the chamber by a load lock. In order to have samples in a capacitor form, the top Al thin film electrodes were deposited onto the plasma polymer thin film samples. Thicknesses of the films have 20nm,100nm,250nm. The capacitance and dielectric loss factor of the plasma polymer thin film samples were measured using Alpha-N Impedance Analyzer (Novocontrol Inc.). The measurements were carried out in the frequency range between 10^{-1} Hz - 10^7 Hz and in the temperature range between 193 K - 353 K with increments of 10 K.

3.Results and Discussion

3.1 Frequency and Temperature Dependence of Dielectric Constant (ϵ')

Dielectric constant is derived from equation (1),

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (1)$$

Where C is the capacitance of the sample, d is the thickness of the sample, ϵ_0 is the permittivity [3, 29,30]

When the frequency dependent dielectric constant for the thin film with thickness of 20 nm was investigated, it was observed that there were two relaxation mechanisms. One of these mechanisms was observed at frequencies lower than 100 Hz and the other mechanism was observed at frequencies higher than 100 Hz. The dielectric constant is 6 at room temperature at 100 kHz as shown in Fig.1.

Fig.1: Frequency and temperature dependence of dielectric constant for 20 nm thickness sample.

Similarly, two relaxation mechanisms are observed for 100, 250 nm. However, the border between two relaxation mechanisms shifts toward higher frequencies from 100 Hz. For 100 nm thickness sample the border is at 1kHz while it is at about 10 kHz for 250 nm thickness sample. The dielectric constants are 13 and 14 from 100, 250 nm thickness samples as shown in Fig.2 and Fig.3.

Fig.2: Frequency and temperature dependence of dielectric constant for 100 nm thickness sample.

Fig.3: Frequency and temperature dependence of dielectric constant for 250 nm thickness sample.

When the effect of temperature is investigated, it is observed that temperature has a rising effect on dielectric constant at all frequencies for all samples.

Sharp drops are detected for the mechanism observed at lower frequencies. This large reductions at dielectric constant may be the results of changing polarizability of large oligomer which are the large residues of PEO backbone as a result of plasma polymerization. The polarization of these large chain components are called as α -relaxation [31,32]. This relaxation shifts toward lower frequencies with decreasing temperature. At higher frequencies at room temperature another mechanism is observed. It is think that this mechanism appears because of the polarization of free radicals originated from side chains and main chain of PEO and small oligomers. This mechanism is called as β -relaxation [31,32]. β -relaxation can be observed at lower frequencies by decreasing temperature.

3.2 Frequency and Temperature Dependence of Dielectric Dissipation ($\tan\delta$)

Dielectric dissipation is the ratio between dielectric loss and dielectric constant as shown in equation (2),

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \quad (2)$$

where ϵ'' is dielectric loss which referres to the energy spent to interaction between polarized charges and the structure, ϵ' is dielectric constant which referres to the polarization of the charges in structure [33].

The presence of α and β relaxation can be observed from frequency and temperature dependent $\tan\delta$.

α -relaxation can be observed only at temperatures higher than 293 K as shown in Fig.4. β -relaxation can be observed at lower temperatures as observed at frequency and temperature dependence of dielectric constant.

Fig.4: Frequency and temperature dependence of $\tan\delta$ for 20 nm thickness sample.

The presence of α -relaxation can be observed at temperatures higher than 283 K and 263 K for 100 and 250 nm thickness samples, respectively.

Fig.5: Frequency and temperature dependence of $\tan \delta$ for 100 nm thickness sample.

Fig.6: Frequency and temperature dependence of $\tan \delta$ for 250 nm thickness sample.

The amplitudes of α -relaxation are greater than of β -relaxation. This difference supports the interpretation indicating that the relaxation mechanism observed at lower frequencies, higher temperatures is α -relaxation and the mechanism observed at higher frequencies, lower temperatures is β -relaxation [34,35].

3.3 Thickness Dependence of Dielectric Constant (ϵ')

It is observed that dielectric constant decreases with decreasing thickness at room temperature as shown in Fig.5. Similar behavior can be observed for all temperatures.

Fig.5: Thickness dependence of dielectric constant (ϵ') at room temperature

When the thickness dependence of $\tan\delta$ is investigated, it is shown that the α -relaxation shifts toward lower frequencies with decreasing thickness. Thus, α -relaxation can not be detected at

20 nm in the investigated frequency range while it can be observed at 250 nm as shown in Fig.6.

Fig.6: Thickness dependence of dielectric loss factor ($\tan\delta$) at room temperature

Plasma polymers have the ability to hold to any substrates well due to the free radicals. This good adhesion ability is more difficult to adapt to the applied electric field change of these surfaces due to the good adhesion of the molecular groups on the surfaces of the plasma polymers that are in contact with the carrier surfaces compared to other molecular groups. These surfaces are called dead layers. Since the contribution of dead layer to total polarization will be more pronounced, the samples with low thickness will have lower polarization ability than thicker samples [36-39].

Conclusion

Plasma polymer thin film samples at different thicknesses were deposited at 5 W plasma discharge power. When the frequency, temperature and thickness dependence of dielectric constant and $\tan\delta$ were investigated, it was observed that there were two relaxation mechanisms in the investigated frequency range. These were called as α and β relaxations. These relaxations shifts toward higher frequencies with increasing temperature. Besides, α -relaxation starts to appear at different temperatures. This shows the difference between the polarizability abilities of samples at same temperature and frequencies. The reason of this behavior can be expressed by dead layer concept which is a result of good adhesion of the bottom layer of plasma polymer to the substrate. When the investigations in this work were concerned, Plasma PEO thin films can be useful as coverage of optical devices such as lenses, visors etc.

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