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Spectroscopic Characteristics of Polymeric Surfaces Modified by DC Glow Plasma Treatment

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Abstract
In this work, a low-pressure dc glow discharge plasma was generated and diagnosed using the electric probing method. Three different gases (Ar, N_2, and SF_6) were used to generate the discharge plasma. The generated plasma was used to treat the surfaces of thin films of polymeric materials (polycarbonate and polymethyl metha acrylic) prepared by solution cast method. The treatment process was performed at different treatment times. The optical and spectroscopic characteristics of the treated surfaces were introduced and compared to untreated surfaces. Results showed reasonable modifications in the surfaces as their transmittance and refractive index have changed with treatment time. Also, the surfaces treated with SF_6 gas showed better characteristics than those treated with Ar and N_2.

Keywords: Infrared Microscopy Analysis; Amyloid Peptide; Free-Electron Laser; Synchrotron-radiation
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1. Introduction

Over the last four decades, polymers have been used successfully in many industrial applications, including adhesion, packaging, thin films, biomaterials, and coatings [1]. Polymers have become a very important material in modern manufacturing processes and offer a wide variety of chemical, optical and mechanical properties applicable to numerous applications [2]. We have used thermoplastic polymers in this study. These are linear, one-dimensional polymers, which have strong intermolecular covalent bonds and weak intermolecular Van der Vaal bonds [3]. A growing interest in polymer applications in such fields as coatings, adhesion, composites, biomaterials, medicine, microelectronics, and thin-film technology requires special surface properties that could be tailored by flame treatment, radiation grafting, chemical treatment, photon irradiation, corona discharge and plasma treatments, as well as ion-beam modification [4]. In order to understand different polymers and their properties, which are usually classified into three groups: thermoplastics, elastomers and thermosets [5]. Thermoplastics are linear or weakly branched polymers with negligible entanglement. They can be crystalline or amorphous [6]. Those, which crystallize, do not form perfect crystalline materials but instead are semi-crystalline with both amorphous and crystalline regions. Polymers in which chain motion is greatly restricted by a high degree of cross-linking [7]. Damage events such as ionization and recoil displacement result in the modification of the original polymer structure [8].

During the last decade plasma has been extensively investigated due to the possible application in technology, synthesis and processing of polymeric materials and spectroscopy [9]. If the surface of a plastic can be non-destructive altered down to a depth of just a few molecules, it can make a profound difference in the practice's suitability for a broad range of applications [10]. Using a cold gas plasma reactor to design the surface by just a few angstroms is a very energy-efficient, clean and environmentally safe green method to change the basic polymer film properties in many applications [11]. Between the possible effects of plasma treatment on a polymer material may be included improved wettability, induced chemical reactivity, improved adhesion to coatings and matrices, hydrophobic properties, cleaning or disinfections [12].

In this study, plasma produced by dc glow discharge. The net effect of the electromagnetic field is to cause electrons to be removed from a reduced pressure gas near any electrodes. The same imposed field through the remaining gas and loose energy then accelerates these stripped electrons by collision

with gas molecules. Thus, there are forming a variety of active species including additional electrons, free radicals, ions and neutral atoms [13]. Any substance inserted into this plasma will be subjected to bombardment by these species and the kinetic or potential energy these products contain [14]. The study only concerns with the type of plasma produced by strong electromagnetic field, in which the effective temperature of the larger ionized gas molecules is only a few tens of degrees [15]. The free electrons in this plasma have relatively high energies (10-20 eV) and at these energies the electrons are of sufficient energy to ionize neutral gas molecules causing the visible glow commonly observed in these systems [16]. Taking into account the position of the two electrodes, they are placed within the reactor. The installations in this category is utilized to induce or to modify some properties and to obtain new polymer materials by polymerization or grafting [17-20].

In the plasma surface modification process, evacuating a reaction chamber and then refilling it with a low-pressure gas create low discharge plasma [21]. The gas is then energized by direct current. The energetic species in gas plasma include ions, electrons, radicals, metastables, and photons in the short-wave UV range [22]. Surfaces in contact with the gas plasma are bombarded by these energetic species and their energy is transferred from the plasma to the solid [23]. A wide variety of parameters can greatly affect the physical characteristics of plasma and subsequently affect the surface chemistry obtained by plasma modification [24]. Processing parameters, such as gas types, treatment power, treatment time and operating pressure, can be varied by the user; however system parameters, such as electrode location, reactor design, gas inlets and vacuum are set by the design of the plasma equipment [25]. This broad range of parameters offers greater control over the plasma process than that offered by most high-energy radiation processes [26-28].

Bond scissoring and cross linking are the main result of high energy ion interaction with the polymer surface. These reactions induce structural modification and change in physical properties [29]. Cross linking occurs when two radicals produce on the neighboring polymer units. The relative molecular mass of the macromolecule increases which result in increase of melting point [30]. Along with the cross linking, degradation also occurs by chain scission which leads to decrease in a molecular mass. Grafted polymer can be produce when, for example, at the polymer backbone radical sites are formed which react with monomers present as a liquid or vapor [31]. The cross linking or scissoring efficiency not only depends on polymer structure but also on the characteristics of radiation sources, ion energy and ion specie [32-34].

2. Experimental Setup

The use of low-pressure plasmas enables the modification of polymer materials. Various plasma components such as electrons, ions, radicals, meta-stables, as well as UV radiation are involved in this reaction processes. These components interact with the exposed surfaces. Since some parts of the surfaces are exposed to energies higher than the characteristic bonding energy of polymers, these parts undergo scission reactions and form new bonding configurations on the surface. Hence every plasma treatment, ablation and deposition, e.g. the generation of new functionalities on polymer surfaces, simultaneously takes place as elementary processes. Depending on the dominating process, which can be influenced by the parameter set, in the end either etching or coating will dominate. While the substrate and the reactor dependent parameters are often predefined, the treatment must be optimized by controlling the material flow into the reactor and by adjusting energy input into the plasma phase. Often an etch-step is performed prior to a deposition process, in order to remove weak boundary layers, and to produce radical sites on the surface [35]. Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites at the surfaces, which are subjected, to post-reaction [36].

The PC films were exposed to N_2,Ar and SF_6 plasma. The plasma is almost as homogenous in a low-pressure glow discharge. In the plasma surface modification process, evacuating a reaction chamber and then refilling it with a low-pressure gas create low discharge plasma. The gas is then energized by direct current. The energetic species in gas plasma include ions, electrons, radicals and meta-stables photons in the short-wave ultraviolet (UV) range. The DC glow discharge is generated by applying a high voltage between two electrodes in the presence of magnetic field at low energy with time variation.

PC has been obtained in the pellet form. In the present study the films were prepared by solution-cast method [37]. It is usually important in dissolving Polymers to have the material as finely divided as possible and to have each particle thoroughly wetted by the solvent. Agitation of some kind is important, since the solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle, which retards further solvent diffusion into the polymer. Starting by calculation the polymer membrane mass by finding the volume of the membrane as follows:

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$V=\pi.r^2.t$ (1)

Where r is the radius of Petri dish in (cm) and t is the thickness of membrane in cm, knowing the density of polymer, one can find the required mass:

Mass = Density x Volume

The PC pellets were dissolved in dichloromethane (CH_2C1_2 -99%) separately and a 5% solution was prepared. The stirring is used for 10 hours, the solution was then put into flat-bottomed Petri dishes. The Petri dish containing solution was floated on mercury to ensure the uniformity in the thickness. The solvent was allowed to evaporate slowly over a period of 20-24 hours in the dry atmosphere. The films so obtained were peeled off and dried in vacuum at 50°C for 2 hours in order to ensure the removal of the solvent. The thickness of the films was 30 to 70 nm with tolerance of ±5 µm.

Typical configuration of a complete plasma processing system is constituted by a stainless-steel plasma cylinder reactor with 40 cm length and 30 cm diameter, electromagnetic energy (DC generator), an adjustment system, high voltage power supply along with milliammeter and high voltage voltmeter to record the dc-discharge current and the discharge high voltage respectively. The SF_6 gas have been selected in plasma processing because it consider as anti-bacteria agents, this leads to use plasma treated PC membranes in different biological and medical applications. SF_6 plasma can change the PC membrane properties from hydrophilicity nature to be high hydrophobicity surface. Furthermore, SF_6 plasmas were more effective in improving the performance of medical grade PC films [38,39]. The negatively-charged metallic grid shown in Fig. (1) was used to repelled the electrons and accelerates the positive ions to impact with PC membrane.

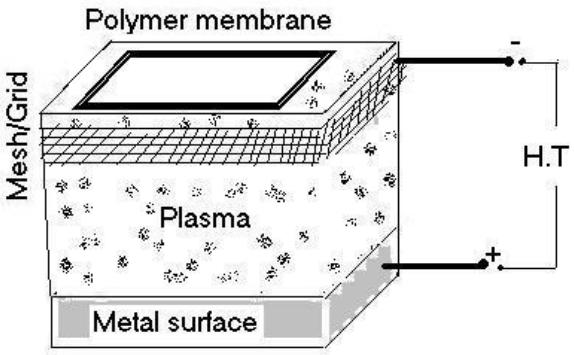


Fig (1) Experimental setup of discharge DC-Plasma

The PC membrane was treated by N_2, Ar and SF_6 plasma at various exposure times and different output power. Different values of the discharge power can be varied by adjusting the input current. The experimental conditions used during the plasma treatment were as follows: Initial gas pressure10^{-4} mbar, working pressure $3x10^{-2}$ mbar, discharge voltage is 4 kV, discharge current is 4 mA, and the discharge power is 16 W. The polymer samples were located at the midpoint of the chamber with the help of glass support. In this work, we have used PC films for plasma treatment.

The polymer films were characterized by optical microscope, UV-visible spectroscopy, laser Ellipsometry and FTIR. Ellipsometry is a nondestructive optical technique that allows one to determine the thickness of, e.g., organic thin films with subnanometer sensitivity in the surface normal direction and the optical constants (refractive indices of the material). In practice, a monochromatic light beam with known state of polarization (e.g., linear polarization) is reflected off the sample surface in specular reflectance. Here one can define an angle of the incoming light as θ, the plane spanned by the incident and reflected light defines the p plane, while the s-plane is perpendicular to that plane. The state of polarization is changed for p-polarized light in a different manner from that of s-polarized light, resulting in an elliptical polarization of the reflected light.

Ellipsometry measures this change in polarization of the reflected light. The reflected light is characterized by two reflection coefficients, R_s and R_p, respectively. In the experiment one determines the ellipsometry angles ψ and Δ that are related to the ratio of R_p and R_s

$$\tan(\Psi)\, e^{i\Delta} = \frac{R_p}{R_s} \quad (2)$$

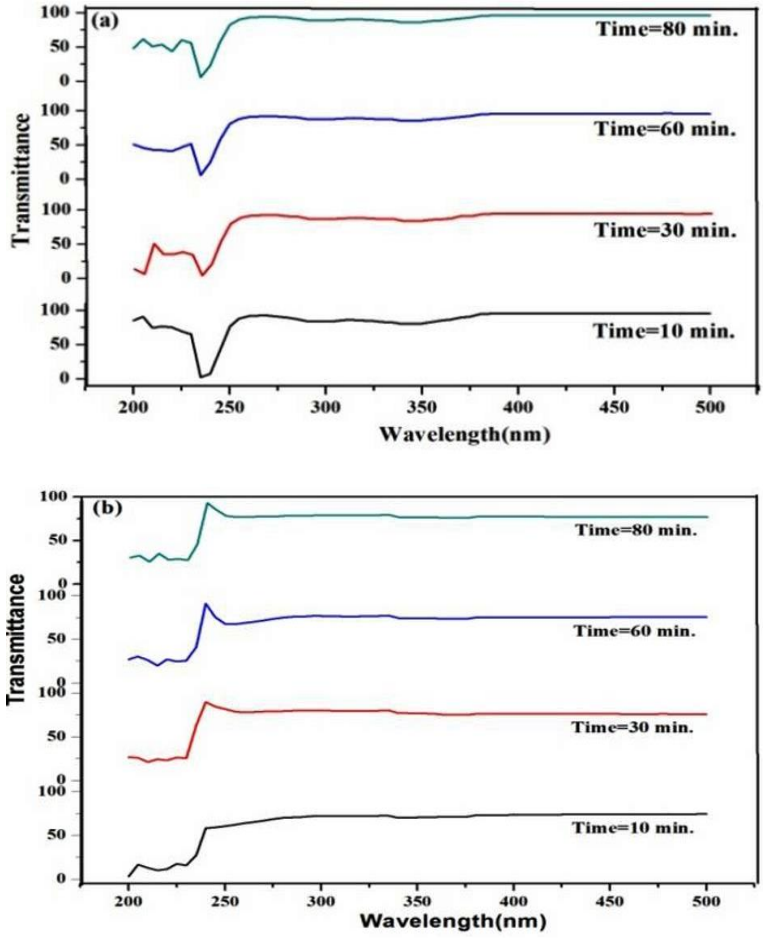
The measurement can be performed in different measurement schemes, namely null-ellipsometry, rotating analyzer or rotating polarizer, as well as phase-modulation mode. Variations of the wavelength and the angle of incidence generate sufficiently large data sets that can be used to calculate the required

data. These calculations are based on an optical model that accounts for all the layers that are present in the sample. Typically, the experimental data are fitted to the model to obtain, e.g., the best-fit value for the film thickness. For thin organic films on solid supports the refractive index of the film material must be known to calculate the desired thickness. The high accuracy of ellipsometry is based in part on the measurement of the ratio of the two values of the reflection coefficients [40-42].

To study optical properties of PC membranes, a UV-visible spectroscopy manufactured by HITACHI model U-2900 spectrophotometer in the wavelength range of 200 nm to 500 nm. To study polymer membrane refractive index and thickness, a SENTECH Carl-Scheelie-str16 Laser ellipsometer.

3. Results and Discussion

The optical transparency for treated PC films was evaluated by recording the UV-visible transmission spectra for various treatment time of nitrogen, SF6 and argon plasma, as shown in Fig. (2), the reference used for transmission measurements is untreated PC film. It is well known that the transparency of a bulk film strongly depends on the surface roughness and an increase in the average roughness will result in a decrease in transmittance due to light scattering effects [43-47]. The increased roughness may be envisioned as the increase in the concentration and sizes of the degradations on surface but the action of some species present in the plasma promotes chain scission (as described in introduction), and this could lead to etching and material removal, thus promoting changes in surface roughness which in most cases positively contributes to a transparency decrease. The increased roughness may be envisioned as the increase in the concentration and sizes of the degradations on surface, which leads to higher light scattering [48,49].This effect shown clearly in PC membrane treated with N_2 and SF_6 plasma. Furthermore, the enhancement in transmittance in spectral region 230 nm of scanning range for argon plasma as in Fig. (2c) referring to formation of sulfur carbonate (SC)-intermolecular layer by cross-linking process, the reference data for SC molecules structure shows high value of the energy gap which can eventually causing emitting of UV photons.



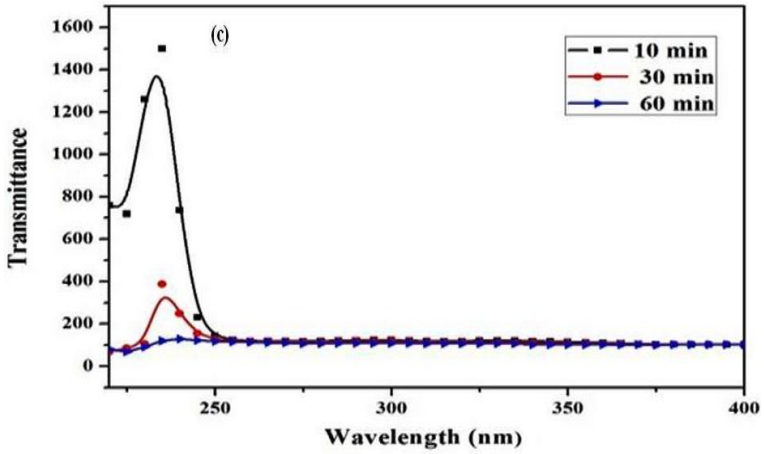
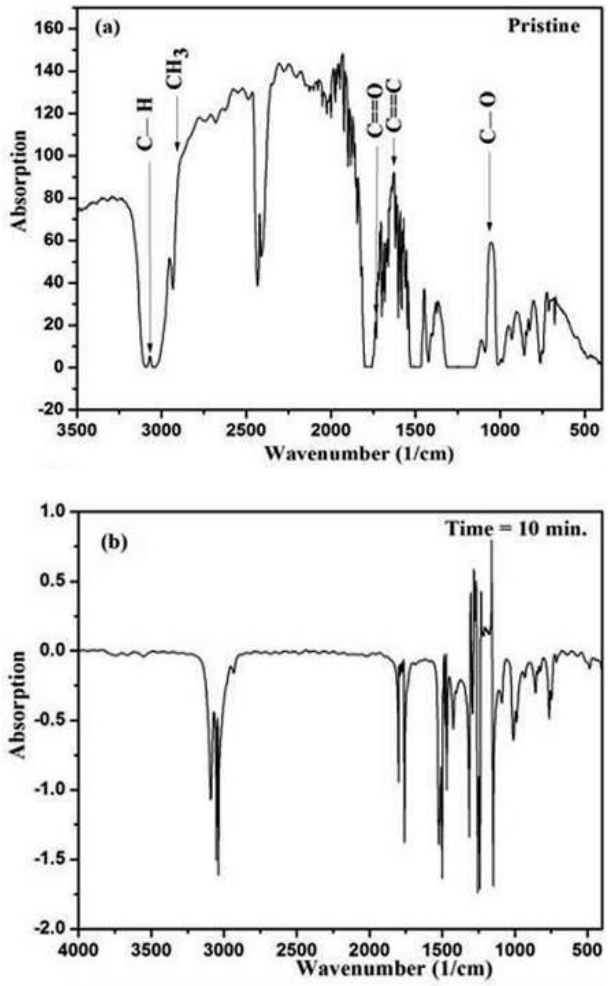


Fig. (2) UV-visible transmission spectra for polycarbonate membranes treated by (a) N_2-plasma (b) SF_6-plasma and (c) Ar-plasma

Plasma treatment by argon ions can break chemical bonds in PC matrix like C-C and C-H, forming free radicals at or near the surface. These radicals tend to be stable by reaction with other radicals [50]. Consequently, recombination process or cross-linking can occur when these free radicals start moving, this interaction can produce high-molecular weight structures.



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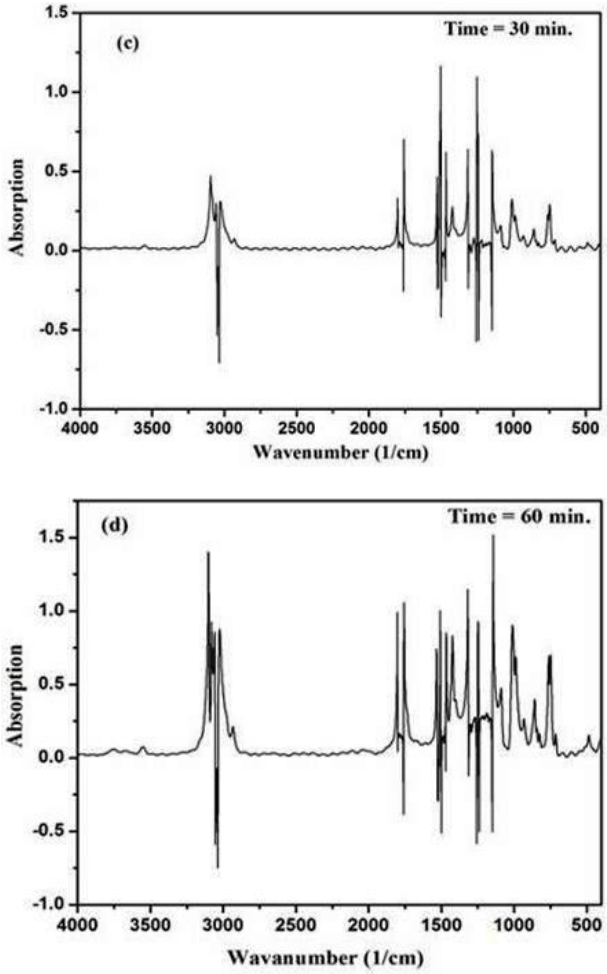

Fig. (3) FTIR spectra for polycarbonate film treated by Ar plasma (a) untreated, (b) 10 min treatment (c) 30 min treatment and (d) 60 min. treatment

The absorption bands as obtained from the untreated film are classified as (a) 1030 cm^{-1}, C-O stretching vibration (b) 1645 cm^{-1}, C=C unsaturated (c) 1770 cm^{-1}, C=O stretching vibration (d) 2890 cm^{-1}, CH_3 stretching vibration and (e) 3070 cm^{-1} C-H stretching vibration of aromatic compound. The enhancement in the absorption bands of C-O and C=O at 1030 cm^{-1} and 1770 cm^{-1} for 10 min, 30 min and 60 min treatment duration has been attributed to the creation of unsaturated –C=C−bonds at 1645 cm^{-1}. It is also observed from FTIR spectra in Fig. (3) that there is decrease in C-C and C-H bands after plasma treatment. It indicates that cross linking phenomenon enhance during plasma treatment.

The initial contact angle values of the untreated PC were 84° and 88° for water and glycerin, respectively. As shown in Fig. (4), these values are rapidly reduced after plasma treatment to be around 47° and 59° for water and glycerin respectively. This behavior has been observed in similar polymers [51-53] for short exposure time. This value is hydrophilic for the PC surface; the reason for this behavior could be a loss of water soluble and short-chained species on the surface [54]. The main effect of the nitrogen plasma treatment is surface functionalization by insertion of different polar groups. The different species present in a nitrogen plasma, such as N_2^+, N_2 (excited), N, N^+, electrons, UV radiation [55,56], interact with the outermost region of the polymer film and promote the formation of a large amount of free radicals, which play a relevant role in the functionalization process since they act as insertion points of active species.

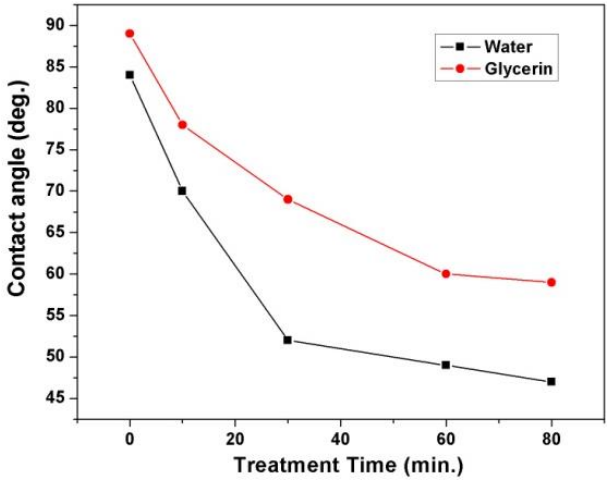

Fig. (4) The change of contact angle of PC films as a function of treatment time using nitrogen plasma for dist. Water and Glycerin respectively

Figure (5) shows the variation of refractive index of PC membranes related to Ar-plasma treatment time of 10 and 80 min.

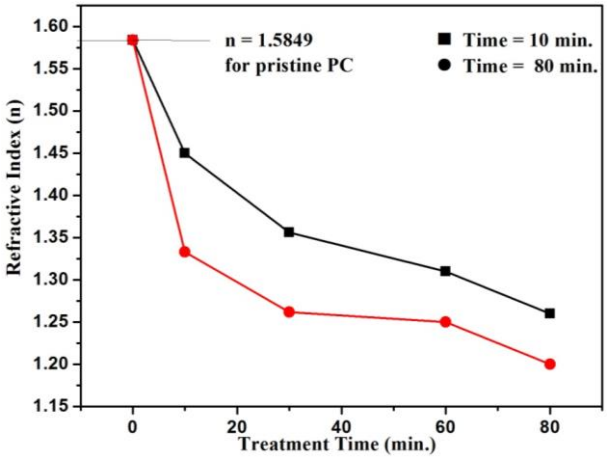

Fig. (5) Ellipsometry measurements for refractive index with plasma treatment time for PC films

4. Conclusion

In this work, a low-pressure dc glow discharge plasma was generated and diagnosed using the electric probing method. Three different gases (Ar, N_2, and SF_6) were used to generate the discharge plasma. The generated plasma was used to treat the surfaces of thin films of polymeric materials (polycarbonate and polymethyl metha acrylic) prepared by solution cast method. The treatment process was performed at different treatment times. The optical and spectroscopic characteristics of the treated surfaces were introduced and compared to untreated surfaces. Results showed reasonable modifications in the surfaces as their transmittance and refractive index have changed with treatment time. Also, the surfaces treated with SF_6 gas showed better characteristics than those treated with Ar and N_2.

References

[1] S.D. Lin, M. Bollinger, and M.A. Vannice, Catal. Lett. 17, 245 (1993).
[2] M. Valden X. Lai, and D.W. Goodman, Science 281, 1647 (1998).
[3] M.M. Shubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Pluzak, and R.J. Behm, J. Catal. 197, 113 (2001).
[4] O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 1(2) 3-8 (2008).
[5] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J.K. Nørskov, J. Catal. 223, 232 (2004).
[6] Z. Yan, S. Chinta, A.A. Mohamed, J.P. Fackler, and D.W. Goodman, Catal. Lett. 111, 15 (2006).
[7] T.V.W. Janssens, B.S. Clausen, B. Hvolbæk, H. Falsig, C.H. Christensen, T. Bligaard, and J.K. Nørskov, Top. Catal. 44, 15 (2007).
[8] B. Hvolbæk, T.V.W. Janssens, B.S. Clausen, H. Falsig, C.H. Christensen, and J.K. Nørskov, Nanotoday 2, 14 (2007).
[9] O.A. Hamadi, N.J. Shakir, F.H. Hussain, Bulg. J. Phys., 37(4), 223-231 (2010).
[10] Y. Zhou, N.J. Lawrence, L. Wang, L. Kong, T-S. Wu, J. Liu, Y. Gao, J.R. Brewer, V.K. Lawrence, R.F. Sabirianov, Y-L. Soo,

 ISSN (print) 2958-8960 (online) xxxx-xxxx Printed in IRAQ

X.C. Zeng, P.A. Dowben, W.N. Mei, and C.L. Cheung, Angew. Chem. Int. Ed. 52, 6936 (2013).
[11] B. Hammer and J.K. Nørskov, Nature 376, 238 (1995).
[12] O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 3(1) 23-26 (2010).
[13] B. Hammer and J.K. Nørskov, Adv. Catal. 45, 71 (2000).
[14] T. Bligaard and J.K. Nørskov, Electrochem. Acta 52, 5512 (2007).
[15] O.A. Hammadi and N.E. Naji, Iraqi J. Appl. Phys., 10(2) 27-31 (2014).
[16] J.G. Wang and B. Hammer, Phys. Rev. Lett. 97, 136107 (2006).
[17] D. Matthey, J.G. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Lægsgaard, B. Hammer, and F. Besenbacher, Science 315, 1692 (2007).
[18] T. Fujitani and I. Nakamura, Angew. Chem. 50, 10144 (2011).
[19] O.A. Hammadi, W.N. Raja, M.A. Saleh and, W.A. Altun, Iraqi J. Appl. Phys., 12(3), 35-42 (2016).
[20] O.A. Hammadi, W.N. Raja, M.A. Saleh and W.A. Altun, Iraqi J. Appl. Phys., 12(4), 19-28 (2016).
[21] I.X. Green, W. Tang, M. Neurock, and J.T. Yates, Jr., Science 333, 736 (2011).
[22] D. Widmann and R.J. Behm, Angew. Chem. Int. Ed. 50, 10241 (2011).
[23] A. Visikovskiy, H. Matsumoto, K. Mitsuhara, T. Nakada, T. Akita, and Y. Kido, Phys. Rev. B 83, 165428 (2011).
[24] N.S. Phala and E. van Steen, Gold Bulletin 40, 150 (2007).
[25] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[26] O.A. Hamadi, Iraqi J. Appl. Phys., 12(2) 9-13 (2016).
[27] R.L. Kurtz, R. Stockbauer, T.E. Madey, E. Román, and J.L. de Segovia, Surf. Sci. 218, 178 (1989).
[28] Z. Zhang, S-P. Jeng, and V.E. Henrich, Phys. Rev. B 43, 12004 (1991).
[29] S. Wendt, P.T. Sprunger, E. Lim, G.K. Madsen, Z. Li, J.Ø. Hansen, J. Matthyiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, and F. Besenbacher, Science 320, 1755 (2008).
[30] O.A. Hammadi, Phot. Sens., 6(4) 345-350 (2016). DOI: 10.1007/s13320-016-0338-4
[31] C.M. Yim, C.L. Pang, and G. Thornton, Phys. Rev. Lett. 104, 036806 (2010).
[32] Z. Dohnálek, I. Lyubinetsky, and R. Rousseau, Prog. Surf. Sci. 85, 161 (2010).
[33] Y. Kido, H. Namba, T. Nishimura, A. Ikeda, Y. Yan and A. Yagishita, Nucl. Instrum. Methods B 136-138, 798 (1998).
[34] H. Matsumoto, K. Mitsuhara, A. Visikovskiy, T. Akita, N. Toshima and Y. Kido, Nucl. Instrum. Methods B 268, 2281 (2010).
[35] L.P. Zhang, M. Li, and U. Diebold, Surf. Sci. 412/413, 242 (1998).
[36] O.A. Hammadi and N.E. Naji, Phot. Sens., 8(1) 43-47 (2018).
[37] U. Diebold, Surf. Sci. Rep. 48, 53 (2003).
[38] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, and M. Haruta, J. Catal. 202, 256 (2001).
[39] J.S. Muenter, J. Mol. Spectroscopy 55, 490 (1975).
[40] Z. Wang, Y. Zhao, X. Cui, S. Tan, A. Zhao, B. Wang, J. Yang, and J.G. Hou, J. Phys. Chem. C 114, 18222 (2010).
[41] A.A. Hadi and O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 1(2) 23-26 (2008).
[42] M. Klimenkov, S. Nepijko, H. Kuhlenbeck, M. Bäumer, R. Schlögl, and
[43] H.-J Freund, Surf. Sci. 391, 27 (1997).
[44] J.T. Miller, A.J. Kropf, Y. Zha, J.R. Regalbuto, L. Delannoy, C. Louis, E. Bus, and J.A. van Bokhoven. J. Catal. 240, 222 (2006).
[45] O.D. Häberlen, S. Cheong, M. Stener, and N. Rösch, J. Chem. Phys. 106, 5189 (1997).
[46] Y. Xu and M. Mavrikakis, J. Phys. Chem. B 107, 9298 (2003).
[47] R.V. Hardeveld and F. Harog, Surf. Sci. 15, 189 (1969).
[48] Z. Huang, P. Thomson, and S. Di, J. Phys. Chem. Solids 68, 530 (2007).
[49] A. Bongiorno and U. Landman, Phys. Rev. Lett. 95, 106102 (2005).
[50] A.K. Yousif and O.A. Hamadi, Bulg. J. Phys., 35(3) 191-197 (2008).
[51] O.A. Hammadi, Mater. Res. Exp., 8(8), 085013 (2021)
[52] F.J. Kadhim, O.A. Hammadi, and N.H. Muthesher, J. Nanophot., 16(2), 026005 (2022).
[53] Z.H. Zaidan, K.H. Mahmood, O.A. Hammadi, Iraqi J. Appl. Phys., 18(4), 2730 (2022)
[54] O.A. Hammadi, Optik, 208, 164147 (2020).
[55] B.T. Chiad, O.A. Hammadi, F.J. Kadhim, and M.K. Khalaf, Iraqi J. Appl. Phys., 12(3), 17-26 (2016).
[56] O.A. Hammadi, Adv. Sci. Eng. Med., 11(5), 346-350 (2019).

 ISSN (print) 2958-8960 (online) xxxx-xxxx Printed in IRAQ