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Effect of O_2, N_2, Ar, and Ar/O_2 Plasma Treatment on Optical Properties of Polyaniline Films

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Abstract

In the current work, improvement of the optical properties of Polyaniline (PAni) films was investigated using cold plasma technique. Samples were treated with different gases including argon (Ar), oxygen (O_2), nitrogen (N2) and Ar/O_2 mixture using low-pressure dc glow discharge. Films of about 300 nm were fabricated by simple deposition of polyaniline suspension in toluene on glass slides. UV-Vis spectrophotometric measurements of the prepared films showed that plasma treatment resulted in a significant increase in the optical band gap of the films. Plasma treatment was found to increase the band gap energies range from (1.7–1.98 eV) of the untreated films to 1.8-2.42 eV of the treated ones. Exposure to oxygen plasma was found to alter the chemical composition of the films and thus, resulting in a high transmission (over 85%) of the peak centred at 550 nm. This increases the photoelectric performance of the plasma treated polyaniline films

Keywords: Polyaniline, Polymer thin films, Plasma treatment, Surface modification, Optical properties

1. Introduction

The study of low-temperature plasma processing has been stimulated and excited by many current and potential applications. The demand for material quality and properties, and the increasing need for materials with new properties, are some of the factors that have given impetus to plasma induction and plasma-based technologies in the industry (1, 2). Today, one possesses a whole gamut of industrial applications where the use of plasma-based technologies provides distinct advantages over other traditional technologies. Some of these apps may be listed as follows: etching, sputtering, plasma polymerization, surface modification, plasma immersed ion implantation, flat plate displays, high-pressure arcs and jets. Organic polymers (PE, PP, PANi, PMMA, PTFE, PET, etc.) are important materials in micro and nanoscale engineering, especially for industrial biological and medical applications (3, 4). Polymer thin films have been used as biomaterials in the medical field from cardiovascular surgery to plastic surgery (5-7). When a biomaterial is implanted into a living tissue, it results in a series of host reactions that take place at the interface between the tissues and the materials. Exposure to a discharge of electricity or plasma is a common practice to improve the surface chemistry of polymer materials. This practice has been used to improve the adhesion, wetting, printability, and biocompatibility properties of materials. Polyaniline (PANi) and its derivatives, which are perhaps the most common conductive polymers, have been generally concentrated because of their great conductivity, electrical properties, and ecological dependability (8-12). This study talks about optical properties

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(refractive index, extinction coefficient, band gap) of untreated polymer films and exposed with Ar, O_2, N_2 and Ar /O_2 mixture gases using dc discharge plasma, which were characterized by spectroscopic ellipsometry.

2. Experiment

In a typical synthesis, polymer solutions with concentrations of 1 gm dissolved in 30 ml of Toluene solution (C_7H_8) and stirred for 5 mins with a magnetic stirrer at temperature of 30 °C. After that, the prepared solution is converted into a sealed glass container and leaves for 24 hours at room temperature where PAni Films consist green color with thickness of 300 nm. The experiments were carried out in Ar, O_2, N_2 and Ar /O_2 mixture plasma produced by a dc discharge in a planer electrodes system. Ar/O_2 gaseous mixture is taken as operational gas, and Ar contribution in Ar/O_2 mixture is 80%. The operating conditions used for obtaining dc discharge plasma are given in table 1. The neutral pressure inside the vacuum chamber was controlled by a needle valve and a vacuum voltage was applied between the cathode and the anode with the anode kept grounded for 20 minutes. The measurements of optical properties for untreated PAni films and those treated with different gases utilizing UV-Visible Recording spectrophotometer (Shimadzu 1700 UV-2601 PC, program 1650) was made in Japan.

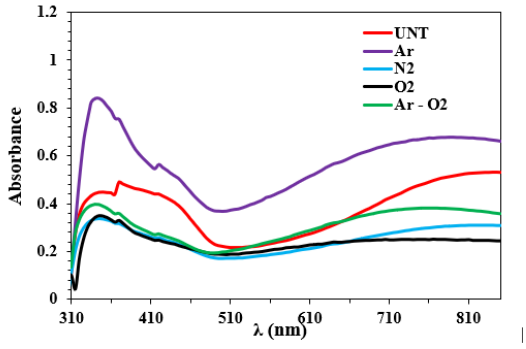

Figure 1. Absorption spectra of untreated PAni films and those treated with different gases.

3. Results and Discussions

Figure 1 shows the absorption spectra of the untreated- and plasma-treated polyaniline films for T= 20minute. The spectral lines for samples treated with the three gases have nearly the same behavior as that for the untreated sample. Figure 1 shows, the spectral lines have peaks of maximum absorbance in the range (310- 410 nm) corresponding to n→σ* transition, as π→π*and n→π* transitions need relatively low energy and, hence, occur at higher UV absorbance for the treated samples were observed. Moreover, the spectral lines of the treated samples showed increased broadening, the samples exposed to plasma have the broadened line and its peak shifted to the shorter wavelength. These changes in the optical absorption indicate that the plasma irradiation induced some chemical and structural changes in the polyaniline polymer films. The amplitude of the spectral lines may be attributed to the presence of extra advances from more elevated levels of ground-state vibration to higher sub-levels of the originally energized single state (13). This behavior is similar to that reported for many polymeric materials exposed to different kinds of radiation such as, ion and electron beams, UV and Gamma radiation. Raia V.N. et al. (14) attributed these changes to the induced formation of conjugated dienes $(-C=C-)_n$ groups through unsaturation of the polyaniline polymer chain. The peaks of absorption spectra that lie in the wavelength range 320-420 nm, which the intensity starts to decrease. Mortazavi et al. (15) attributed this decrease to the loss of carbonyl compound (C = O) which may be due to the oxidative decomposition of the double bonds' plasma or etching effect on the surface of the substrate. The increase followed by a decrease in the UV-Vis absorbance peak for polyaniline polymer films upon plasma treatment, attributed such behaviour to the decrease in the number of radicals due to crosslinking (14-17).

Table 1: DC discharge operating conditions used for obtaining plasma treatment.

Parameter	Values Applied
Working Pressure	8 x 10^{-2} mbar
Inter-electrode spacing	5 cm
Applied power	700 Volt
Flow rate of gas	40/min
Exposure time	20 min
Working gas	O_2, N_2, Ar ,Ar/O_2

Figure 2 shows, the transmittance spectra, obtained at room temperature and near normal occurrence of pristine film and different gases exposing the plasma in the visible region. It was found that the permeability decreased, this is due to the fact that an increased

concentration of granules causes a higher light scattering (18). As can be seen, the films obtained have a higher transfer of 60% for 500 nm which are exposed to oxygen plasma. The optical transmittance at wavelength of 300-800 nm decreases for films treated with Ar and N2 plasma. This is due to the reactive yield of etching Ar and N2 plasma is less than oxygen plasma which related to highly absorbing nature of the polymer material. As shown in Figure 3, the absorption coefficient can be calculated from the following mathematical expression (19):

$$\propto = \frac{2.303}{d}\ log_{10}(\frac{1}{T}) \qquad (1)$$

Where d is the film thickness and T is the permeability.

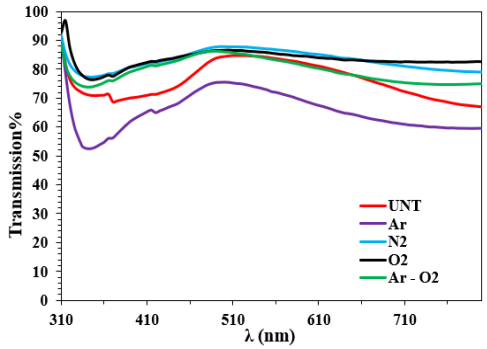

Figure 2. Transmission spectra for untreated and PAni films with Ar, O2, N_2 and Ar /O_2 gases mixture plasma.

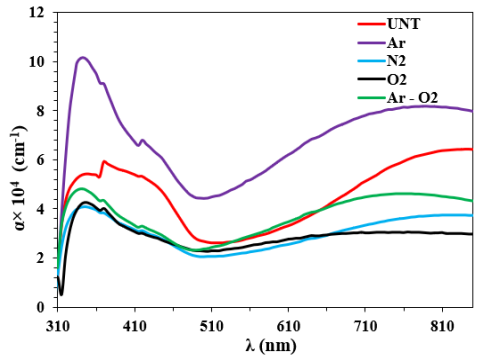

Figure 3. Absorption coefficient for untreated and PAni films with Ar, O2, N2 and Ar /O2 gases mixture plasma.

Refractive indices of the films were predicted before and after plasma treatment. Results showed the decrease of the refractive indices(n) decreases with the energy of the photon upon exposure to different plasmas. Exposure to oxygen plasma has a higher effect on the spectral dependence of (n) on the wavelength of the films as shown in Fig.4. The refractive index decreased in all spectral range (230–830 nm) with the plasma treatment except the Ar treatment. Reducing polymer crosslinking or increasing the bond strength in the plasma polymer network could be responsible for this behavior.

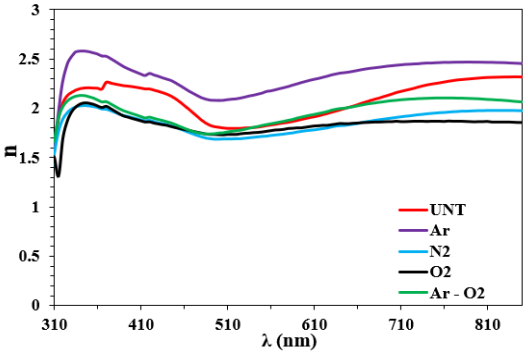

Figure 4. Refractive index for untreated and PAni films with Ar, O_2, N_2 and Ar /O_2 gases mixture plasma.

The transmission of the air / polymer interface T is expressed as function of the refractive index (n) and the extinction coefficient (K) and calculated by means of equation (20).

$$T = \frac{4n}{(n+1)^2+K^2} \qquad (2)$$

Once the measurements of T values, an iterative procedure to calculate n and K is initiated. When the absorption α is known, the extinction coefficient K can be found the relation:

$$K = \propto \frac{\lambda}{4\pi} \qquad (3)$$

Where λ the wavelength of light.

The variance in extinction coefficient decreases with the wavelength, and after 500 nm, it has a large increase in the contrast. Because of the property of transparency, PAni's thin films may be a strong candidate for coating in organic photovoltaic devices such as LEDs and lenses (17).

Generally, in ideal crystalline materials, no energy gap transition occurs. However, in amorphous materials, the transitions from the extended states occupied for the valence band to the empty tail states of the conduction band, and from the tail states occupied in the valence band, to the hollow extended states of the conduction band, may occur. The optical

band gap, Eg, associated with the amorphous nature of the material, can be calculated from the equation of Davis and Mott (21, 22):

$$\propto (\upsilon) = \frac{B(h\upsilon - E_g)^m}{h\upsilon} \qquad (4)$$

Where B is a constant and m is an exponent equal 1/2, 3/2, 2, or 3 according to nature of the electronic transition, whether it is direct allowed or direct forbidden or indirect allowed or indirect forbidden respectively. The value of m can be estimated if one plot $(\alpha h\upsilon)^{1/m}$ versus $(h\upsilon)$, which often yields a straight line fit to the absorption edge. In our case, the best straight-line fit was found for m=1/2 corresponding to a direct allowed transition. An extrapolated $(h\upsilon)$ at which $(\alpha h\upsilon)^{1/m} = 0$ provides a value of the optical band gap Eg.

The calculated Eg values of the studied films are listed in Table 2.

Table 2: The optical parameters of untreated and plasma-treated polyaniline films.

Sample	A	T%	α (cm^{-1})	K	n	ε_r	ε_i	Eg (eV) $(\alpha h\nu)^2$	Eg (eV) $(\alpha h\nu)^{1/2}$
untreated	0.44	71.39	53211	0.178	2.194	4.782	0.781	1.98	1.7
Ar	0.56	64.96	68120	0.228	2.355	5.493	1.073	2.42	1.93
N_2	0.26	82.16	31030	0.104	1.878	3.516	0.390	2.7	2.45
O_2	0.25	82.66	30060	0.101	1.862	3.456	0.374	2.9	2.2
Ar(80)-O_2(20)	0.27	81.16	32969	0.110	1.910	3.636	0.421	1.8	1.58

4. Conclusions

It can be concluded that, exposure of polyaniline films to Ar, O_2, N_2 and Ar/O_2 gases plasma results in a significant increase in their optical energy gaps. Therefore, plasma-treated polyaniline films are considered to be potential for manufacture of electronic/optoelectronic devices because of their high transparency and their wide band gap in the visible region of the light.

5. Conflicts of interest

"There are no conflicts to declare".

6. Formatting of funding sources

Self

7. Acknowledgments

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