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Effect of Ar bombardment on the electrical and optical properties of low-density polyethylene films

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Abstract.   The influence of low-energy Ar ion beam irradiation on both electrical and optical properties of low-density polyethylene (LDPE) films is presented. The polymer films were bombarded with 320 keV Ar ions with fuences up to 1×10^{15} cm^{-2}. Electrical properties of LDPE films were measured and the effect of ion bombardment on the DC conductivity, dielectric constant and loss was studied. Optically, the energy gap, the Urbach's energy and the number of carbon atoms in a cluster were estimated for all polymer samples using the UV–Vis spectrophotometry technique. The obtained results showed slight enhancement in the conductivity and dielectric parameters due to the increase in ion fluence. Meanwhile, the energy gap and the Urbach's energy values showed significant decrease by increasing the Ar ion fluence. It was found that the ion bombardment induced chain scission in the polymer chain causing some carbonization. An increase in the number of carbon atoms per cluster was also observed.

1. Introduction

Polymers are available in   different compositions, forms and properties because of which they can be widely used in different applications. The modifications induced in the properties of polymers by radiation are used in a wide range of applications such as strain sensing applications, optical display [1], polymer light-emitting diode [2], electronic devices [3], electrical biosensing and solid-state battery. Low-density polyethylene (LDPE) is one of these polymers which can be used in several industrial and bioengineering applications [4]. Low-energy ion beam bombardment is a powerful tool for modifying near-surface region of the polymers producing materials with unique properties for wide applications in microelectronics and

sensors to medicine and space [5–7]. Ion beam irradiation of polymers induces changes in the physical properties of these polymers, which is a result of energy deposition by incoming ions within the materials. These changes are accompanied by the formation of free radicals, carbon–carbon multiple bonds, cross-linking, chain scission (–C–C– bond scission) and volatile species [8]. These alterations lead to changes in optical, dielectric and electrical properties of irradiated polymers [9–13]. The ion beam bombardment of polyolefin (like LDPE) causes formation of polar groups on the irradiated surface polymer, and therefore it is imperative to study the influence of induced dipoles on both the dielectric and optical transitions within the irradiated LDPE films [14]. One method for

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a thorough knowledge of the induced transition and also for getting information about the optical and electrical changes in the irradiated polymer, is to study the optical and electrical properties, especially, the dielectric parameters and the absorption band edge.

The main objective of this study is to investigate the effect of Ar ion beam irradiation on the electrical and optical properties of LDPE by measuring the conductivity, dielectric constant and loss, resonance frequency, relaxation time, band-gap energy and Urbach's energy to be used in suitable applications. The Ar ion fluence varies from 1×10^{13} ions·cm^{-2} to 1×10^{15} ions·cm^{-2}. The induced modification of the electrical properties of the irradiated samples was correlated by the change in the optical band gap. For more information, an attempt has been made to correlate the obtained results with the reported data.

2. Experimental work

Low-density polyethylene (LDPE) pellets manufactured in Exxon Chemical Company were used. The polymer density is about 0.935 g cm^{-3} and its degree of crystallinity is about 45%. Isotropic films of 1 mm thickness were obtained by compression molding at 433 K and 15 MPa, followed by quenching by immediately transferring to the water-cooled press under the same pressure. The LDPE films were bombarded with argon (Ar) ions of 320 keV energy. The ion implanter was a Balzers MPB 202 RP type, located at the Institute of Electronic Material Technology, Warsaw, Poland. Ion bombardment was done to all samples at room temperature. The beam density was adjusted below 0.1l μA cm^{-2} to avoid the increase in temperature of the surface layer of the films. The bombardment of LDPE films was carried out in vacuum, where the pressure was in the order of 10^{-4} Pa. The range R of 320 keV Ar ion, nuclear energy loss ($S_{\rm n}$) and electronic energy loss ($S_{\rm e}$) in 1 mm of LDPE sample are calculated by SRIM 2008 [5] and are equal to 486.5 nm, 196 eV/nm and 466.5 eV/nm, respectively. The electrical properties were measured using a locally designed electrical circuit [11]. Two electrodes

were fixed at the opposite surfaces of each films using silver paste to ensure good electrical contacts. The DC resistance of LDPE films was measured using a digital electrometer from Keithley (type 6517A), USA. Meanwhile, Hioki LCR bridge of the type 3532 Z Hi-Tester from Japan was used for measuring the AC parameters. The frequency range was selected to be from 200 Hz to 5 MHz with an accuracy range of 0.15–4%. The bridge was connected to a PC using an interface of type Rs-232c. All electrical measurements were carried out at room temperature in the Department of Basic Engineering Science, Faculty of Engineering, Menoufiya University, Egypt. The spectrophotometer used in this study for the UV–Vis measurements was of type UV2 double beam supplied by Unicam, England. The measurements were performed in the wavelength range from 190 to 1000 nm, where the resolution was selected to be 1 nm. LDPE films were carefully cleaned before the optical measurements. The films were placed in a metallic holder of 1×1 cm dimensions for the transmission of the beam through the centre of the films. The air was chosen as the reference. The optical measurements were performed at the Atomic Energy Authority (AEA), Egypt.

3. Results and discussions

3.1 *Electrical properties*

The electrical conductivity ($\sigma_{\rm DC}$) values, under direct current, for the pristine and ion-bombarded LDPE samples are given in table 1. From the table, one can clearly observe the slight increase in the value of $\sigma_{\rm DC}$, due to ion bombardment upto a fluence of 1×10^{14} cm^{-2}, where its value was 7.85×10^{-10} ($\pm 2\%$) Ω^{-1} m^{-1} for the pristine film and increased up to 1.18×10^{-9} ($\pm 2\%$) Ω^{-1} m^{-1} for the 1×10^{14} cm^{-2} bombarded film. Then, the value of $\sigma_{\rm DC}$ seems to be constant for the highest fluence ion bombarded film. This slight increase in $\sigma_{\rm DC}$ can be attributed to the chain scission of the macromolecules induced by ion bombardment [15]. The increase in the polymer conductivity is generally due to either the increase in the number of free charges or

Table 1. DC conductivity ($\sigma_{\rm DC}$), relaxation time (τ) and resonance frequency ($\omega_{\rm c}$) as functions of Ar ion beam fluence.

Fluence (ions/cm^2)	$\sigma_{\rm DC}$ (Ω^{-1} m^{-1})	τ (s)	$\omega_{\rm c}$ (Hz)
Pristine	7.85×10^{-10}	2.585×10^{-6}	386832.2
10^{13}	9.75×10^{-10}	2.68×10^{-6}	373250.2
10^{14}	1.18×10^{-9}	2.959×10^{-6}	337940.6
10^{15}	1.18×10^{-9}	3.13×10^{-6}	319152.3

the enhancement of the mobility of the electrons and/ or holes already existing in the polymer. Both processes occurred in the bombarded films, as the chain scission induces a decrease in the average molecular weight of LDPE. This, in turn, leads to an increase in the molecular mobility. Moreover, the scission can reduce the number of valence electrons in the polymer, where the number of free charges may increase as a result of this scission. Therefore, the value of σ_{DC} is increased for the bombarded samples. Meanwhile, the highest fluence $(1 \times 10^{15} \text{ cm}^{-2})$, may tend to a saturation value for such scission so that no more scissions could be occurred in the polymer chains. Therefore, σ_{DC} value remains constant. The dielectric parameters of all LDPE films have been determined, and the dielectric constant (ε') and dielectric loss (ε'') were calculated using these parameters.

The raw dielectric data were fitted by applying the Debye's equations [16,17]:

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + \omega^2\tau^2}, \tag{1}$$

$$\varepsilon'' = \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{1 + \omega^2\tau^2}, \tag{2}$$

where ε'_∞ is the minimum value of the dielectric constant at the end of the frequency range, ε'_s is the dielectric constant at static field, $\omega = 2\pi f$, f is the frequency and τ denotes the relaxation time. From eqs (1) and (2), a linear equation is obtained, which relates the dielectric parameters as

$$\varepsilon''/\omega = (\varepsilon' - \varepsilon'_\infty)\tau. \tag{3}$$

Equation (3) can be written in a logarithmic form as follows:

$$\log(\varepsilon''/\omega) = \log(\varepsilon' - \varepsilon'_\infty) + \log(\tau). \tag{4}$$

The intercept of the straight line in eq. (4) represents the logarithm of relaxation time τ. The values of the relaxation time are listed in table 1 for the pristine and irradiated samples. These values exhibit slight increase with increase in ion fluence. The increase in relaxation time with increase in fluence might be due to the increase in the total surface area of the polymer molecules [17], which, in turn, increases the capability of the charge storage inside the bombarded films. Substituting the values of τ in both eqs (1) and (2), one can get fitted values of both ε' and ε''. Figure 1 represents the variation of dielectric constant with both ion fluence and the frequency at the 200 Hz–5 MHz range. A dipole relaxation trend was observed in all the LDPE films in this spectrum. The spectra of all samples can be divided into three regions. The first one lies in the low-frequency range (200 Hz–7 kHz). In this region, all samples show slight decrease in the dielectric constant values with the frequency. Also, it is noticed that the ion bombardment induces an increase in the values of ε' when the fluence increases. The second region represents the relaxation region, where a sharp decrease is observed in ε' values as the frequency increases up to ~300 kHz. Here, one can observe that the resonance frequency values show some decrease with increasing Ar ion fluence. In the last region (from 300 kHz to 5 MHz) ε' exhibits a slight decrease with increase in frequency values. In this region, there is
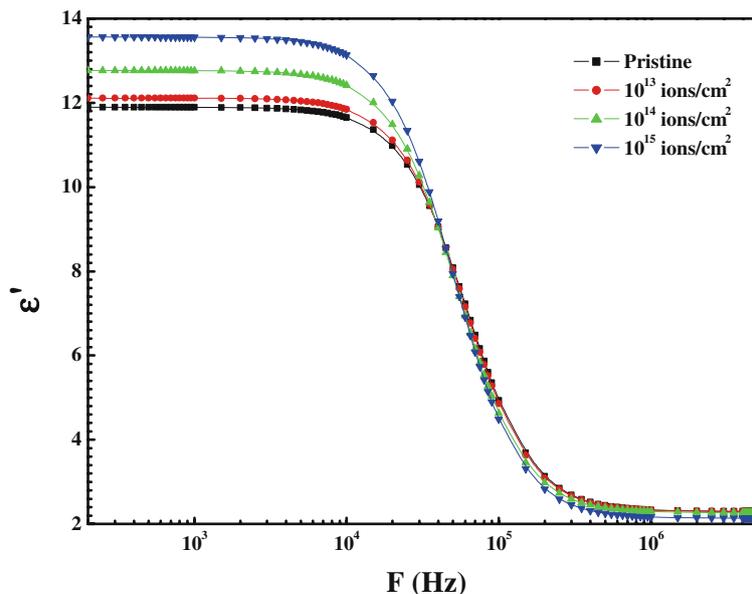

Figure 1. The dielectric constant as a function of frequency for the pristine and 320 keV Ar ion-bombarded LDPE films.

no significant change in ε' values with increase in ion fluence. The increase in ε' could be ascribed to some enhancement in the quantity of the dipoles inside the polymer film due to ion bombardment. These dipoles could be arisen from ion bombardment, where they are normally C–O and/or C=O groups [18]. Although the irradiation was introduced to LDPE films in vacuum ambient, the free radicals formed due to ion bombardment could interact with air after irradiation when the samples are exposed to air.

A dipole relaxation is also observed during the dielectric loss (ε'') measurements. Figure 2 shows the relation between ε'' and the frequency of the full range (200 Hz–5 MHz) for the pristine and ion-bombarded samples. All samples show loss peaks with maxima at the resonance frequency (ω_c). The resonance frequency, here, represents the reciprocal of the relaxation time. The value of the peak maximum was found to slightly increase with increasing ion fluence. Moreover, the position of the peak, and in turn the value of ω_c, was found to shift, due to irradiation, towards lower frequency. However, the dipole relaxation behaviour is preserved even after the ion bombardment of LDPE films. This agrees well with the trend of the dielectric constant ε'. One can assume that some defective states (traps) can be formed inside the band gap of the bombarded films that can be filled with charge carriers [19,20]. The resonance frequency (ω_c), was calculated for all samples and listed in table 1. The molecules or atoms show maximum dispersion at ω_c. It was found that ω_c is slightly decreased from 386.83 kHz

(the pristine film) to 319.152 kHz, if the film was bombarded with Ar beam of 1×10^{15} cm^{-2} fluence.

Figure 3 shows the logarithmic dependence of the total conductivity ($\log(\sigma_T)$) on the logarithmic frequency ($\log(\omega)$) for all the films. The conductivity behaviour is directly proportional to the frequency. However, no significant change was found in the values of the conductivity due to irradiation. The exponent factor of the universal power law of the conductivity was obtained for all films. Its value was ranged between 0.84 and 0.98, indicating that all samples exhibit hopping conduction mechanism [21].

3.2 *Optical properties*

The absorption spectra for all polymer films were obtained in 200–1000 nm wavelength range (shown in figure 4). It is clearly seen that the absorption edge was found to shift monotonically towards longer wavelengths as the ion fluence increases. This shift can be attributed to the formation of some unsaturated groups as a result of ion bombardment [22]. This matches very well with the electrical measurements. The absorption coefficient (α) is an important parameter for the characterization of the optical properties of a material. It can be calculated from Urbach' formula [23] as

$$I(t) = I_0 e^{-\alpha t}, \tag{5}$$

where $I(t)$ is the intensity of the polymer of thickness t, while I_0 is the intensity of the incident beam. Tauc's equation [24] relates α to the absorbed photon energy ($h\nu$) as follows:

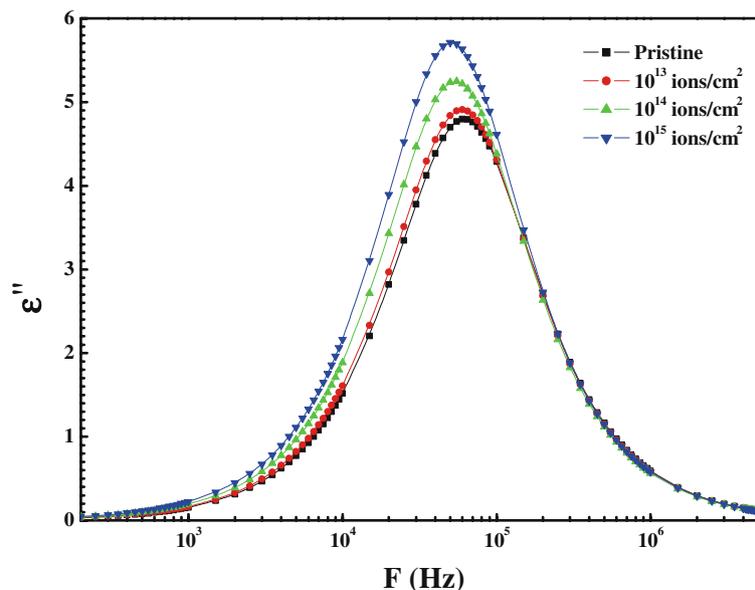$$\alpha h\nu = A(h\nu - E_g)^n, \tag{6}$$

Figure 2. The dielectric loss as a function of frequency for the pristine and 320 keV Ar ion-bombarded LDPE films.
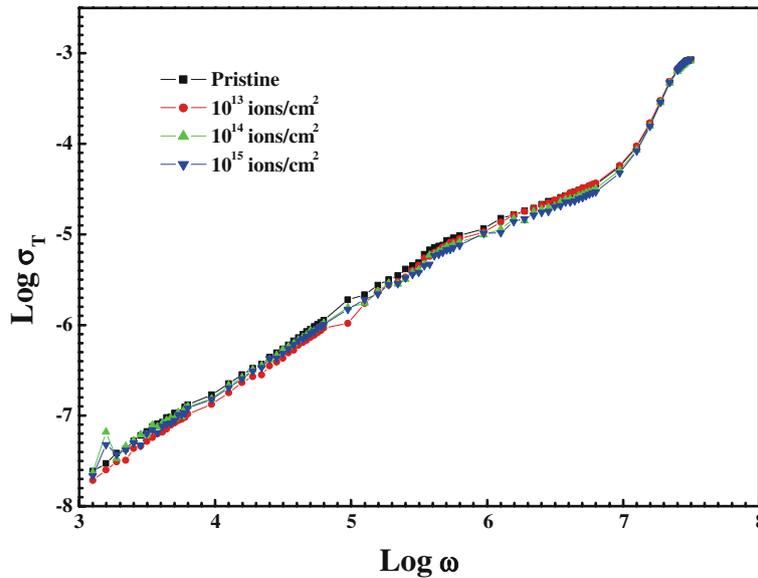
Figure 3. The logarithmic variation of the total conductivity vs. the angular frequency for the pristine and 320 keV Ar ion-bombarded LDPE films.

where A is a constant and E_g represents the optical energy gap. The index n is a good indicator of the transition type, where it may be equal to 1/2, 3/2, 2 or 3. For this study, n takes the value of 1/2, where it gives good linearity as shown in figure 5. This value is attributed to the allowed direct transition. The values of E_g were obtained from figure 5 by the intercept of the extrapolation of the linear part in the absorption spectra, where $\alpha = 0$ in eq. (6). Figure 6a is a plot of E_g vs. the ion fluence for LDPE films. It is obvious that an inverse proportion is obtained between the ion bombardment and the energy gap of LDPE samples. This

decrease in E_g typically was found to be from 4.2 eV for the pristine film to 3 eV for the 1×10^{15} cm^{-2} bombarded film. The decrease in energy gap with the highest ion fluence was about 29% from its original value. This decrease may be attributed to the formation of intermediate levels with increase in ion fluence; this is due to irradiation. Also, it can be attributed to the formation of carbon-enriched clusters due to the release of hydrogen as hydrogen molecules [25]. It is well known that the number of carbon atoms within the cluster depends on the optical energy gap. Robertson and Reilly [26] found that the number of carbon atoms
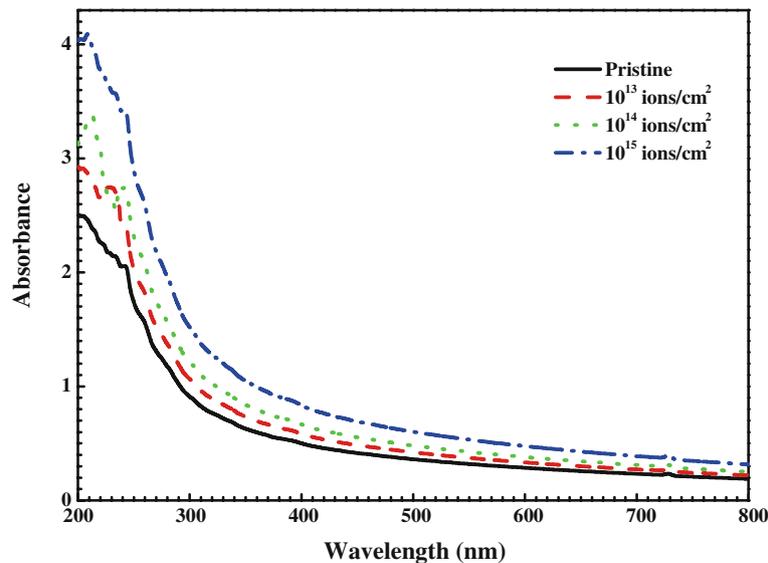

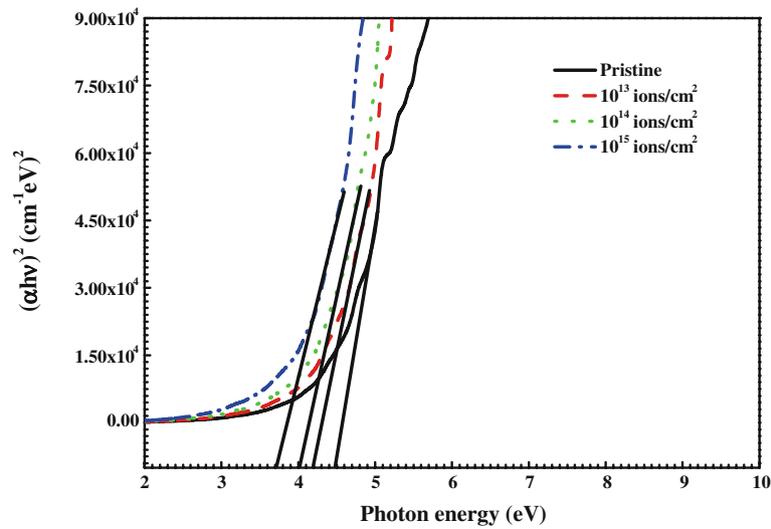**Figure 4.** UV–Vis spectra for the pristine and 320 keV Ar ion-bombarded LDPE films.

Figure 5. Plots of $(\alpha h\nu)^2$ vs. photon energy for the pristine and Ar ion-bombarded LDPE films.
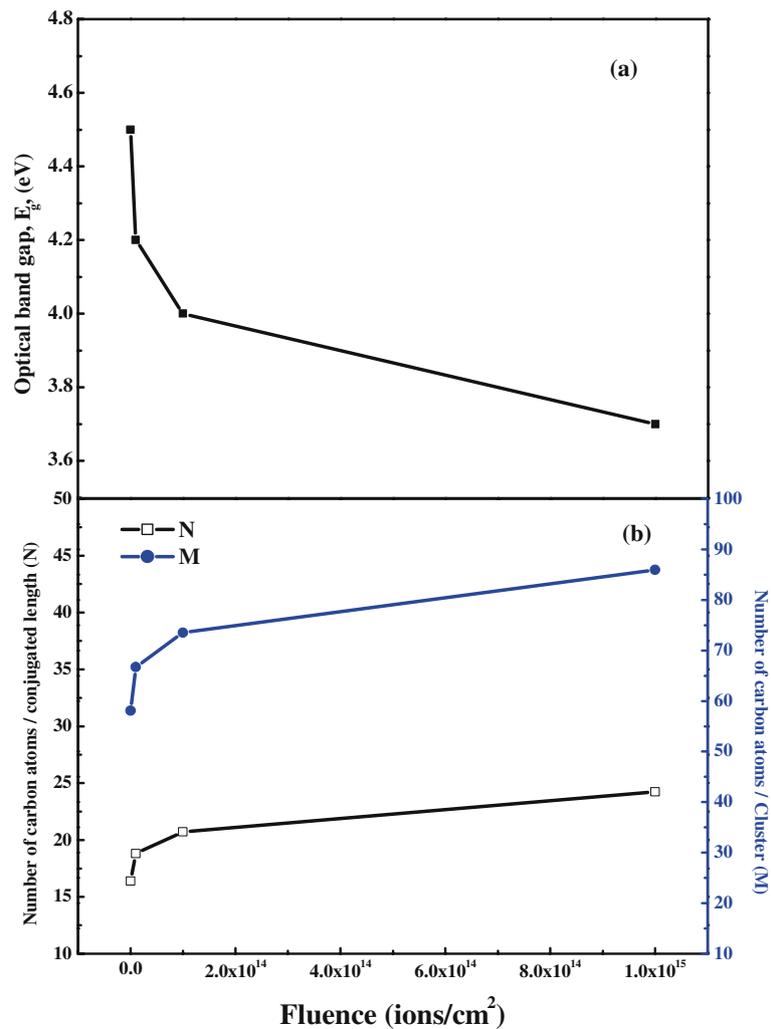

Figure 6. (**a**) Dependence of the energy gap E_g values and (**b**) the number of carbon atoms per conjugated length N and clusters M on the Ar ion fluence for LDPE films.
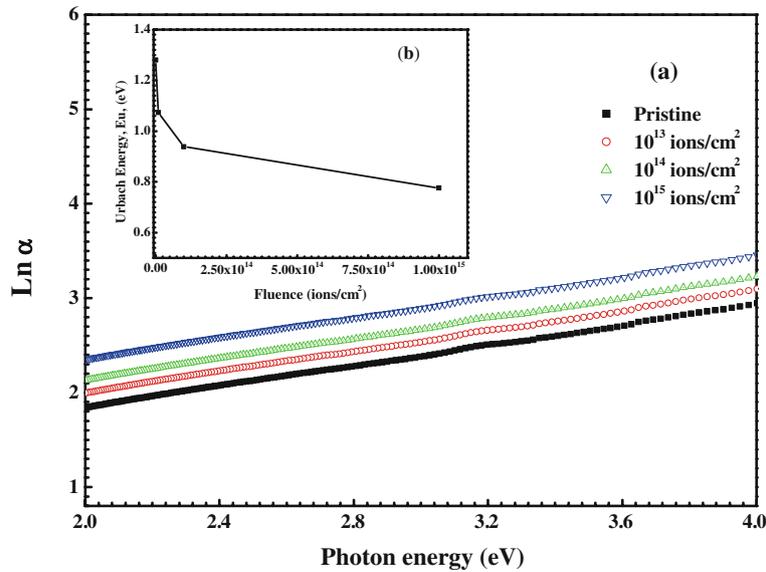
Figure 7. (**a**) The logarithmic variation of the absorption coefficient (α) against the photon energy for the pristine and ion-bombarded LDPE films and (**b**) the Urbach's energy as a function of ion fluence.

per conjugated length (N) inside the cluster can be estimated by the relation:

$$E_g = 2\pi\beta/\sqrt{N}, \tag{7}$$

where 2β is the band structure energy of a pair of adjacent π sites. β takes the value -2.9 eV for a 6-membered carbon ring. However, Robertson relation was used to estimate the cluster size for the bombarded polymers. Robertson relation was modified by Fink *et al* [27], where they assumed the cluster structure to be like buckminsterfullerene (C_{60} rings instead of C_6). If M represents the number of carbon atoms in a cluster, one can relate this number to E_g by the following relation:

$$E_g = 34.3/\sqrt{M}. \tag{8}$$

It is clear from figure 6b that the values of both N and M increase with the increase in ion fluences, which can be attributed to the formation of an array of conjugate bonds after irradiation of the polymer material. The optical Urbach's energy (E_u) of the pristine and bombarded LDPE films is generally calculated from the band tail. One can use the Urbach's relation as follows:

$$\alpha = B\exp(h\nu/E_u). \tag{9}$$

The reciprocal of the slopes in figure 7a represents the values of E_u, where the linear relation is clear between $\ln \alpha$ and $h\nu$ for all LDPE films. It was found that the Urbach's energy decreases with increase in Ar ion beam fluence. The relation between E_u and ion fluence is shown in figure 7b. From the figure, one can see that the trend of E_u agrees well with that of E_g results.

4. Conclusion

The ion bombardment showed some significant changes in both the electrical and optical behaviour of LDPE films. The irradiation-induced conjugated double bonds (C=C) could be the reason for the decrease in the bandgap energy and Urbach energy. This could also be the reason for the slight enhancement of the conductivity of LDPE films. Meanwhile, both the dielectric constant and loss show significant increase that might be due to the formation of some dipoles over the polymer surface such as C–O and C=O as a result of the exposure of the polymer films to the air after Ar ion bombardment. The number of carbon atoms per conjugated length as well as the number of clusters showed an increase due to ion bombardment of the polymer films, which assures the carbonization of the polymer. This result shows that the ion irradiation is an effective method to improve the surface of polymers so that they can be used as conductive surfaces in microelectronic appliances.

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