Improved surface properties of PTFE polymer films using broad ion source

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The main objective of this paper is to improve the surface properties of the polytetrafluoroethylene (PTFE) polymer films by ion beam irradiation with 2 keV Ar⁺ energy and various ion fluence ranging from 1×10^{17} to 3×10^{17} ions/cm². Various characterization techniques, namely, X-ray diffraction (XRD), UV-Vis spectroscopy and electrical measurements have been used to confirm these changes. XRD measurement shows the decrease of the XRD peak intensity and reflects some loss of crystallinity after irradiation. The UV-Vis has shown a shift of the absorption edge of irradiated samples towards the visible region. The band gap energy E_g was calculated using Tauc's relation, and its value decreases with an increase of ion fluence for all irradiated samples. Increasing ion fluence leads to slight increase in electrical conductivities (σ_{dc} and σ_{ac}) and dielectric loss ε_2 for PTFE samples.

Keywords: PTFE, Ion beam, SRIM, Structural, Optical, Electrical properties

1 Introduction

The improvement of polymer surface properties by ion beam is a subject of widespread importance due to the increasing use of polymers in radiation environments, space crafts, electronic and photonic devices, etc.¹⁻³. The unique properties of PTFE make it suitable for applications where high temperature stability, chemical resistance and low coefficient of friction make it the ideal material. PTFE is linear chain crystalline polymer with structure, highly stable and hardly degradable, when exposed to ionizing radiations such as proton beams, gamma radiation and electron beams⁴⁻⁶. The importance of ion beam irradiation on PTFE is to create more bioactive surfaces, improve the adhesion with metallic films, improve the mechanical, increase the electrical conductivity and improve cell adhesion control for biomedical applications⁷⁻¹². The ion source irradiation technique has proven more effective in modifying PTFE than other techniques because of its higher cross-section for ionization and larger linear energy transfer. This technique also offers the possibility of surface modification occurring not at elevated temperature but usually at room temperature. The energy transfer from ions bombardment to the target

surface material results in a complex combination of polymer cross-linking, covalent bond breaking, chain scission, carbonization, defluorination and formation of free radicals^{13,14}. The interaction degree of ion beam irradiation with the polymer depends on many factors such as the chemical composition, crystal structure, surface morphology and irradiation dose^{15,16}. Some changes in the physico-chemical properties of different number of polymers modified by different ion beams have been studied¹⁷⁻¹⁹. These changes have included changes in crystal structure of PE²⁰, conductivity of PTFE²¹, thermal stability of PI²², wettability of PC and PET^{23,24}, and optical properties of $PADC^{25}$. In our present study the modifications in the structural, electrical and optical properties induced by ion beam irradiation on PTFE have been investigated.

2 Experimental

2.1 Sample preparation

Commercial PTFE films with dimensions of 1×1 cm² were cleaned ultrasonically in acetone, and dried in an oven at 100 °C for 90 min to remove any residual solvent. These samples are supplied from Institute of National Centre for Radiation Research and Technology (NCRRT), Cairo, Egypt.

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2.2 Ion source irradiation system

The PTFE samples were irradiated in a vacuum chamber using locally design broad beam ion source at NCRRT, AEA, Egypt. The ion source consists of a stainless steel cylindrical anode surround by permanent magnet to confine the discharge in the central zone, stainless steel cathode disc are separated by Teflon flange as shown in Fig. 1. A digital positive power supply is used for initiating the discharge between the anode and the cathode that is connected to the earth. Extractor electrode is connected to negative power supply to extracted ion beam and ion collector plate is connected to the earth through a micro ammeter. The ion beam irradiation system is operated under high vacuum which evacuated up to 1×10^{-5} mbar. The conditions used for irradiation in this experiment are pressure 2×10^{-4} mbar, current density 100 A/cm^2 , argon ion energy equals 2 keV and different irradiation time. The beam density was kept as low as possible to prevent rising of the samples temperatures.

2.3 Characterization techniques

After ion beam irradiation, the samples were taken out from the vacuum chamber and analyzed by different characterization techniques. The PTFE films structure were analyzed by fully computerized x-ray diffractometer (Shimadzu XD-6000). The optical band gap and band tail width are determined by measuring the optical properties using UV-Vis spectrophotometer (CECIL 3041, UK) in the wavelength range from 200 to 900 nm. For the dc measurements, a Keithley digital electrometer (6517 A, USA) was used for the determination of the dc resistance of the films. The ac measurements were carried out using the Hioki LCR meter (RS-232 C interface, Japan) operating at a frequency f range (60 Hz-1 MHz). The bridge connected with computer for instrument control and data processing. Each curve data of the optical and electrical measurements was taken as an average from three curves for PTFE samples under the same conditions.



Fig. 1 – Cold cathode broad beam ion source irradiation system

3 Results and Discussion

3.1 SRIM /TRIM simulation

Stopping and range of ions in matter (SRIM) and transport of ions in matter (TRIM) programs are given excellent theoretical information with experimental data for ion penetration depths, defect distributions, phonon distributions, distributions of scattered atoms, and distributions of transmitted ions²⁶.

The Argon ion penetrates into the PTFE polymer films colliding with carbon, and fluorine atoms and they recoil. The recoiled atoms receive energies high enough to leave their sites in the structure and subsequently collide with other C, and F atoms. A tree of collisions forms by a thousand of ions implanting into randomly distributed target atoms as shown in Fig. 2. The final distribution of the positions for the implanted ions come to rest (stopped ions) has a maximum under the modified surface layer as shown in Fig. 3.



Fig. 2 - SRIM codes for 1000 penetrating argon ions in PTFE



Fig.3 – 2 keV argon ions distribution in PTFE

3.2 Structural properties

The XRD technique is used to determine the structure and degree of crystallinity for PTFE before and after irradiation. PTFE can be classified as a semi-crystalline high performance thermoplastic polymer and the degree of crystallinity affects the physical properties of PTFE and is itself affected by the application.

Figure 4 shows the diffraction pattern of the pristine and irradiated PTFE sample with ion beam fluence 3×10^{17} ion/cm². The pattern shows a sharp peak at $2\theta = 17.88^{\circ}$ for the pristine PTFE and shifted to 18.12° after irradiation. Small shift in the peak position of PTFE by ion beam after irradiation implies small changes in the lattice parameters. There is some decrease in the peak intensity by irradiation that indicates some disorder changes in PTFE film. This change may be explained by the relief of residual stress in the amorphous region and the decrease in the probability of entanglement per molecule is caused by radiation induced chain scission²⁷⁻³⁰.

3.3 UV-Vis spectrometry

The UV-Vis technique is used to determine the value of optical band gap and band tail width of PTFE polymer. The PTFE is an insulator polymer, and hence it is used for insulating application. There is attenuation to decrease in the band gap energy of PTFE by ion beam irradiation with different ion beam fluence. This decrease in the band gap energy is quite considerable for optical application.

The relation between the optical absorption coefficient α and the photon energy was given by Fahrenbruch and Bube³⁰:

... (1)



Fig.4 - XRD spectra for the pristine and irradiated PTFE film with 2 keV argon ions

where A is the constant, h is the Plank's constant, v is the frequency of the radiation, and E_g is the optical energy gap as shown in Fig. 5. According to Urbach rule³¹ the optical absorption coefficient α can be calculated as follows:

$$\alpha = \frac{1}{L} \ln(\frac{I_0}{I_t}) \qquad \dots (2)$$

where I_o and I_t are the intensities of incident and transmitted light, respectively, L is the thickness of the sample. For further characterization for the optical behavior of the PTFE, the activation energy (band tail width) values were determined using Urbach rule³¹:

$$\alpha = B \exp(\frac{h\nu}{E_a}) \qquad \dots (3)$$

where B is the constant and E_a is the band tail width which is usually interpreted as the width of the tail of localized states in the forbidden band gap. Figure 6 shows the variation of $ln(\alpha)$ and the photon energy hv at different Ar ion fluence for PTFE films. The values of the band tail width E_a were determined from the slope of the straight line of this relation as shown in Fig. 7.

The band tail width decreases from 1.17 eV for the pristine to 1.15 eV for the irradiated sample with ion beam fluence 3×10^{17} ions/cm² as listed in Table 1. The decrease in the band tail width E_a of PTFE might be associated with formation of clusters of amorphous carbon within the Ar ion irradiated PTFE as confirmed. The clusters of carbon and the some defects bring a higher carrier concentration on band structure. Presence of these defects might lead to



Fig. 5 – Band gap spectra for the pristine and irradiated PTFE films with 2 keV argon ions

the formation of lower-energy states and decrease the gap between the conduction and valence bands for the irradiated PTFE s confirmed with the results of XRD.

Results of the optical energy gap E_g for pristine and irradiated PTFE as a function of ion fluence is shown in Table 1. The results clearly show that the values of



Fig.6 – Band tail width spectra for the pristine and irradiated PTFE films with 2 kev argon ions



Fig.7 – The Number of carbon cluster N, optical band gap energy E_g and band tail width E_a for the pristine and irradiated PTFE films

Table 1–Optical band gap energy E_g , band tail width E_a
and number of carbon cluster N for the pristine and irradiated
PTFE films with 2 keV argon ions

Ion fluence (ions/cm ²)	E_g (eV)	E_a (eV)	Carbon cluster (N)
Pristine	2.54 ± 0.010	1.17 ± 0.008	183±0.50
1×10^{17}	2.50 ± 0.026	2.10 ± 0.015	190±1.30
2×10^{17}	2.39 ± 0.020	1.83 ± 0.010	207±1.15
3×10 ¹⁷	2.44 ± 0.017	1.15 ± 0.026	198±0.90

optical energy band gap E_g decreases with increasing ion fluence. It decreases from 2.54 eV for pristine sample to 2.44 eV for the irradiated sample with ion fluence 3×10^{17} ions/cm² as shown in Fig. 7. The decrease in the optical energy values is due to creation of some charge carriers and carbon clusters which lead to a decrease in optical band gab³².

3.4 Carbonaceous clusters determination

Carbonaceous clusters are supposed to be rich with enhance the charge carriers that electrical conductivity in irradiated polymers ion and consequently they also influence the optical properties of such materials. The number of carbon atoms Nin a cluster is correlated with the optical energy band gap E_g using the following equation³³:

$$E_g \approx 34.4 / \sqrt{N} \qquad \dots (4)$$

Table 1 shows the change in the number of carbon clusters N as a function of ion fluence. One notes that the number of the carbon atoms in clusters increases with increasing the ion fluence as in Fig. 7. This is due to the breakage of C–C bonds with increasing ion fluence³⁴.

3.5 Electrical conductivity

PTFE has outstanding electrical properties that remain stable over an extremely wide range of temperatures and varying environmental conditions. PTFE with its properties like low dielectric constant and loss tangent have many applications in electronic devices. In this section we used electrical measurements techniques to determine the electrical conductivity, dielectric constant and dielectric loss for PTFE before and after ion beam irradiation.

The *I-V* characteristic curve for the pristine and irradiated PTFE at room temperature with applied electric fields up to 200 V and different ion fluence is shown in Fig. 8. The current increases by increasing the applied voltage and by increasing the ion beam fluence. It is suggested that the increase in current for the irradiated samples is due to the formation of clusters with rings or due to the formation of conjugated double bonds and the oxidation process³⁵.

From Fig. 9, it is clear that dc electrical conductivity σ_{dc} is an increasing function of the ion fluence. Such an increase in the conductivity may be explained on the basis of the fact that ion beam irradiation in polymers leads to the formation of free radicals and dangling bonds and release of low

molecular weight volatile species like hydrogen resulting in the creation of cross-linked carbonaceous clusters on the irradiated surface of polymer and provide the continuous path for the charge transfer within the insulating polymer chains³⁶.

Figure 10 shows the increase in the ac conductivity σ_{ac} by ion beam irradiation; this increase may be attributed to chain of the polymer, resulting in an increase of defects in polymer besides formation of conductive islands. When an ac field of sufficiently high frequency is applied to a polymer structure may cause net polarization resulting in higher ac conductivity at higher frequency³⁷.

Figure 11 shows the dielectric constant ε_1 of the pristine and irradiated samples as a function of the frequency. The dielectric constant decreases with the frequency and the ion fluence, this effect confirms the formation of carbons clusters which have heavier ions that no longer able to rotate sufficiently rapidly, so



Fig. 8 - I-V characteristics for the pristine and irradiated PTFE films



Fig.9 – Dc conductivity σ_{dc} as function of frequency *f* for the pristine and irradiated PTFE films

that their oscillations will begin to lag behind those of the field³⁸.

The increase of dielectric loss ε_2 value with ion beam irradiation as shown in Fig. 12 may be



Fig. 10 – Ac electrical conductivity σ_{ac} as function of frequency *f* for the pristine and irradiated PTFE films



Fig.11 – Dielectric constant ε_1 as function of frequency *f* for the pristine and irradiated PTFE films



Fig.12 – Dielectric loss ε_2 as function of frequency *f* for the pristine and irradiated PTFE films

attributed to the formation of defected states resulted from the chain scissions occurring in the band gap of the irradiated polymer. Generally, these defects may result in the existence of traps of the charge carriers in the band gap of the polymer that can capture the charge carriers³⁹.

4 Conclusions

Some techniques like XRD, Ramman spectroscopy, UV-Vis and electrical measurements are used to characterize the structure, chemical, optical and electrical properties of PTFE after irradiated by 2 keV Ar+ ion. By increasing ion beam fluence, a decrease in the band gap energy and band tail width is found. The electrical conductivity and dielectric loss are increased by ion beam irradiation. It was concluded that the ion irradiation is beneficial to induce improvement in the irradiated PTFE films.

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