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## Surface modification and metallization of polycarbonate using low energy ion beam

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## HIGHLIGHTS

- The low energy argon ion is used for irradiation polycarbonate samples.
- The surface roughness increase from 9  $\mu\text{m}$  to 23.5  $\mu\text{m}$  after argon ion irradiated.
- Copper films are deposited onto polycarbonate (PC) substrates.
- Energy band gap decreases from 3.45 eV for pristine to 1.7 eV for copper thin film.

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## ABSTRACT

The low energy argon ion is used for irradiation polycarbonate samples using cold cathode ion source. The surface of the PC substrates is examined using SEM, UV-spectroscopy and FTIR. It was found that the energy band gap decrease by increase argon ion fluence. Copper films are deposited onto polycarbonate (PC) substrates after irradiation by argon ion beam. The structure, surface morphology and the optical band gap are investigated using XRD, SEM and UV spectroscopy. It can be seen that the intensity increases with deposition time and band gap decreases from 3.45 eV for the pristine PC to  $\sim 1.7$  eV for copper thin film.

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## 1. Introduction

Technological demands for low weight, low cost, and large-area Integration have driven the development of stretchable, flexible electronic devices. These devices commonly use polymer materials as substrates, which have the advantages of low density and enhanced stretchability compared to silicon (Si) substrates (Sim et al., 2013). The use of polymer substrates has resulted in new applications including flexible displays (Jin et al., 2009; Katsuhara et al., 2010), solar cells (Krebs et al., 2009) and electrical sensors (Shamanna et al., 2006), demonstrated that the stability and mechanical reliability of such devices are still a challenge. The growth of electrical resistance of thin metal films on polymer substrates was investigated by several groups for copper on Polyimide (Lu et al., 2009; Hu et al., 2011; Niu et al., 2007), Al on Polyimide (Macionczyk and Brückner, 1999; Alaca et al., 2002) and

Ag on PET (Chen et al., 2013). The commercial success of polycarbonate (PC) is due to its unique combination of properties, including high toughness and impact resistance, good thermal stability and large plastic deformation before failure. It is used in various applications including aeronautic, automotive, electrical and telecommunications (Hudgin, 2000). The physical and chemical modifications induced in polymers under ion bombardment. Ion irradiation of polymeric material induces irreversible changes in their macromolecular structure. It can be used to change in a controlled way the physical properties of thin films or to modify the near surface characteristics of a bulk material (Radwan et al., 2008). The aim of this paper is to investigate the effect of ion bombardment on the optical properties of polycarbonate via UV-Vis spectroscopy and deposition of copper over an insulating polymer, which can be utilized in various electrical and electronic applications.

## 2. Experimental details

The polycarbonate film samples about  $1 \times 1 \text{ cm}^2$  and 100  $\mu\text{m}$  thick which were immersed in a dilute detergent solution, rinsed

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ultrasonically in deionized water, and blown dry in N<sub>2</sub> gas before they were introduced into the chamber. It can irradiate these samples with various argon ion fluence using cold cathode ion source at the National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority.

The ion source characteristics.

The output characteristics of the cold cathode ion source is obtained as shown in Fig. 1 at pressure =  $2.5 \times 10^{-4}$  mbar. The operating condition of the ion source in this experiment are; Ar ion beam current;  $I_b=200 \mu\text{A}$ , ion energy is 5 keV, pressure =  $2.5 \times 10^{-4}$  mbar, extraction voltage equals  $-500$  V and ion fluences;  $0.5 \times 10^{18}$  ion/cm<sup>2</sup>,  $1.0 \times 10^{18}$  ion/cm<sup>2</sup>.

Scanning electron microscopy (JEOL SEM5400 at NCRRT) is the most commonly used technique for surface morphology investigation.

Surface Roughness Tester, TR110 is used for measuring surface texture. It is quantified by the deviations in the direction of the normal vector of a real surface from its ideal form.

UV/Vis spectra of the pristine and all the irradiated samples are performed in the wavelength range from 200 to 1000 nm, using the UV-Visible spectrophotometer model CECIL 3041, UK at NCRRT. During the measurements, the PC films are held in a metal holder after cleaning with bi-distilled water, keeping air as a reference. An ATI Mattson (Genesis series, Unicam, England) FTIR spectroscopy is used to scan and measure the transmittance spectra.

In this study the irradiated films are characterized using a fully computerized X-ray diffractometer, Shimadzu XRD-6000. The X-ray tube is operated at 40 kV, 30 mA anode current and Cu radiation  $\lambda=1.54056 \text{ \AA}$  throughout the measurements. The pattern is recorded at a scanning rate of  $8^\circ/\text{min}$ .

### 3. Results and discussion

#### 3.1. Surface morphology

Surface morphology changes are indicated in Fig. 2 for pristine PC and irradiated with ion fluence  $1 \times 10^{18}$  ion/cm<sup>2</sup>. The surface irregularities increase with the increase of ions fluence. An energetic ion passing through the polymer transfers its energy into highly localized regions in a very short time interval through nuclear (elastic) energy loss ( $S_n$ ) and electronic (inelastic) energy loss ( $S_e$ ). In the keV range of ion energy,  $S_n$  is greater than  $S_e$  (Table 1) and lead to creation of atomic size point defects and clusters of defects in the target (Hassan et al., 2015). The damaged zones and

defect clusters are chemically reactive compared to the surrounding region.

The surface roughness values are;  $9 \mu\text{m}$ ,  $15 \mu\text{m}$  and  $23.5 \mu\text{m}$  corresponding to pristine PC,  $0.5 \times 10^{18}$  ions cm<sup>-2</sup> and  $1 \times 10^{18}$  ions cm<sup>-2</sup> respectively.

#### 3.2. FTIR

The FTIR spectrum of polycarbonate samples after irradiated by different ion fluence is show in Fig. 3. It is clear that the transmittance of the FTIR peaks is decreased by increasing ion fluence. The decrease in transmittance intensity is attributed to the cleavage of the carbonate linkage and to the -H abstraction from the backbone of the polymer, associated with the formation of CO<sub>2</sub> and -OH with varied intensities (Nouh et al., 2009). The subsequent decrease at higher fluence indicates cross-linking. The low intensity band at  $2080 \text{ cm}^{-1}$  gradually disappears with increase of fluence.

#### 3.3. UV-spectroscopy

The absorbance spectrum of Polycarbonate samples reveals the shift in spectra towards the visible region (higher wavelength) as shown in Fig. 4. The gradual shift in the absorption edge as a result of ion irradiated may be attributed to the bond breaking, which lead to release of the volatile species from the material, chain scission, free radical formation, cross-linking, defects and formation of new bonds (Singh and Prasher, 2006; Phukan et al., 2003; Mathakari et al., 2008; Abdul-Kader, 2014).

The optical band gap:

The absorption coefficient  $\alpha$  is related to the optical energy gap and the frequency dependence as given by Tauc equation (Tauc et al., 1966);

$$\alpha h\nu = A(h\nu - E_g)^s$$

where A is a constant, h is Planck's constant;  $\nu$  is the frequency of the radiation,  $E_g$  is the optical energy gap and s is an index, which characterizes the electronic transition. The index s takes the values 1/2, and 2 for direct allowed and indirect allowed transitions, respectively.

The direct optical band gap is evaluated from the absorption spectra by the extrapolating the straight line part of the curves  $(\alpha h\nu)^2$  versus  $(h\nu)$  as depicted in Fig. 5 for the pristine and irradiated polycarbonate with argon ions. It is obtained from the figure that the optical energy band gap decreases with increasing ion fluence. This decrease may be attributed to carbon clusters and/or defects formed in PC polymeric material, which increases with increase ion fluence (Abdul-Kader, 2014). The decrease in band gap after irradiation that observed as the visual change in the color of the pristine sample from milky white to black color after irradiated (Abdel-Fattah, et al. 2002; Rizk, et al. 2008; Kumar et al.; 2012).

The optical activation energy:

For further characterization, one can determine the optical activation energy of PC films using the Urbach rule (Abdel-Fattah et al., 2002; Rizk, et al., 2008) as

$$\alpha = B \exp\left(\frac{h\nu}{E_a}\right)$$

where B is constant and  $E_a$  is the activation energy.

The optical activation energy  $E_a$  is easily calculated from the inverse of the slope of the linear part of the curve between  $\ln \alpha(\nu)$  and energy  $h\nu$  as shown in Fig. 6. The values of  $E_g$  and  $E_a$  for all polycarbonate samples are listed in Table 2. It is observed that  $E_a$  decreases with the increasing ion fluence. The decrease in the activation energy due to the formation of carbon clusters resulting

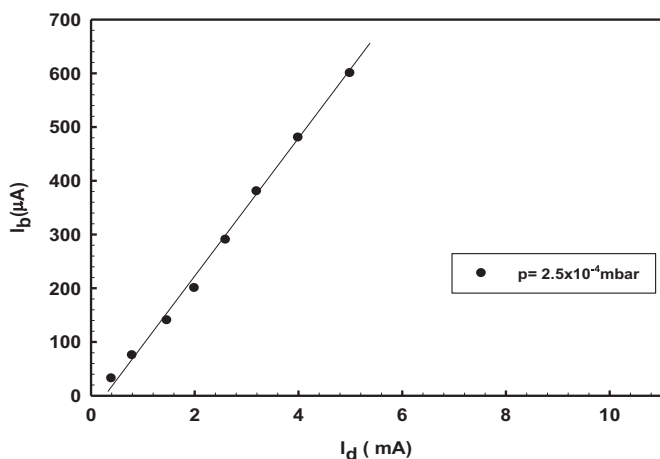


Fig. 1. Variation of output ion beam current with discharge current using argon gas.

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