



Comparative study of metal and non-metal ion implantation in polymers: Optical and electrical properties



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ABSTRACT

The implantation of 1 MeV metal ($^{63}\text{Cu}^+$, $^{107}\text{Ag}^+$, $^{197}\text{Au}^+$) and non-metal ($^4\text{He}^+$, $^{12}\text{C}^+$) ions in a polycarbonate (PC) matrix has been studied in order to evaluate the role of ion species in the modification of optical and electrical properties of the polymer. When the ion fluence is above $\sim 1 \times 10^{13}$ ions cm^{-2} , the threshold for latent tracks overlapping is overcome and π -bonded carbon clusters grow and aggregate forming a network of conjugated C=C bonds. For fluences around 1×10^{17} ions cm^{-2} , the aggregation phenomena induce the formation of amorphous carbon and/or graphite like structures. At the same time, nucleation of metal nanoparticles (NPs) from implanted species can take place when the supersaturation threshold is overcome. The optical absorption of the samples increases in the visible range and the optical band gap redshifts from 3.40 eV up to 0.70 eV mostly due to the carbonization process and the formation of C_{ox} clusters and cluster aggregates. Specific structures in the extinction spectra are observed when metal ions are selected in contrast to the non-metal ion implanted PC, thus revealing the possible presence of noble metal based NPs interstitial to the C_{ox} cluster network. The corresponding electrical resistance decreases much more when metal ions are implanted with at least a factor of 2 orders of magnitude difference than the non-metal ions based samples. An absolute value of $\sim 10^7 \Omega/\text{sq}$ has been measured for implantation with metals at doses higher than 5×10^{16} ions cm^{-2} , being $10^{17} \Omega/\text{sq}$ the corresponding sheet resistance for pristine PC.

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1. Introduction

High-fluence implantation is a unique method for modifying the properties of bulk materials by inducing damages and/or introducing exotic species above their solubility limits. By varying the ion energy, fluence and current it is possible to tailor the nature of the damages and to control the size and density of nanoclusters produced inside the irradiated matrix [1–3]. Novel materials with specific optical, electrical and magnetic properties can be obtained due to the changes of the chemical structure of the matrix and the nucleation and growth of nanostructures starting from the native species through the polymer carbonization [1]. Nevertheless, depending on the incident energy, also the implanted ions tend to aggregate due to their strong cohesive energy giving rise to nanostructures when the supersaturation threshold is overcome [2].

In this framework, keV–MeV ion implantation of polycarbonate (PC) is a prime example of marked modifications induced by ion beams in a polymer especially in terms of optical response as well

as surface/volume resistance [2]. The creation of conducting islands inside the insulating matrix wheatear due to the presence of carbonaceous clusters [4], or of metal nanoparticles (NPs) when metal ions are used as projectiles [5,6], is commonly considered the origin of the electrical conduction achieved through hopping or tunneling between islands [7–9]. In this sense, ion implantation can be seen as a powerful tool for the development of conducting plastics with important repercussions in the field of flexible electronics, electrical bio-sensors [8] and strain, pressure or bending sensing technology [1].

In this study all the implantation processes were carried out by using 1 MeV ions in order to be in the middle between the so-called low and high depth ion implantations, in a regime where electronic energy losses (inelastic collision, S_e) are not dominant on the nuclear energy ones (elastic collision, S_n) [1], thus suggesting that the damage process could not completely overwhelm the cluster nucleation of the implanted species [10]. This means that the implantation process of metallic species can result more advantageous in term of conductivity enhancement.

In a previous work we demonstrated that the 1 MeV $^{63}\text{Cu}^+$ irradiation of PC matrices induces a drastic increase of the electrical conductivity with up to 10 order of magnitude reduction of the sheet resistance with respect to the pristine polymer [10]. These

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results were in good agreement with chemical modifications observed in terms of C–O single bonds breakage, C=O and –C=C– double bonds and –C≡C and ≡CH triple bonds formation. In this work, we irradiated PC matrices with 1 MeV metal ($^{63}\text{Cu}^+$, $^{107}\text{Ag}^+$, $^{197}\text{Au}^+$) and non-metal ($^4\text{He}^+$, $^{12}\text{C}^+$) ions in a range of fluences from 5×10^{13} ions cm^{-2} to 2×10^{17} ions cm^{-2} , in order to estimate how the nature of the implanted species affects the final optical and electrical properties of the polymer. The changes induced in the absorption spectra in the range 400–800 nm and, correspondingly, in the optical band gap are correlated to the electrical resistance as obtained from current–voltage (I–V) characteristics in suitable Van der Pauw configuration.

2. Experimental

1 mm thick amorphous PC matrices (Makrofol-KG, $\text{C}_{16}\text{H}_{14}\text{O}_3$, is an aromatic polymer with density of 1.2 g cm^{-3} , derived from Makrolon GP resin) were purchased from Bayer AG [11]. Different ion implantation processes were carried by using a 3 MV 4130HC Tandemron accelerator (High Voltage Engineering Europa B.V.) at CEDAD – Center for DAting and Diagnostics of the Department of Engineering for Innovation, University of Salento [12,13], keeping constant the beam energy, namely 1 MeV, but using different species: $^4\text{He}^+$, $^{12}\text{C}^+$, $^{63}\text{Cu}^+$, $^{107}\text{Ag}^+$, $^{197}\text{Au}^+$. The whole set of implantations were carried in vacuum at a pressure of 1×10^{-7} mbar, scanning the 2 mm diameter ion beam on the sample surface by an electrostatic X–Y beam scanning unit. The current density was kept constant at 40 nA cm^{-2} for ion fluences $\leq 5 \times 10^{15}$ ions cm^{-2} and at 90 nA cm^{-2} for all the other samples, with an implantation rate of 4.5×10^{11} ions $\text{cm}^{-2} \text{ s}^{-1}$ for fluences $\leq 7 \times 10^{16}$ ions cm^{-2} and of 23×10^{11} ions $\text{cm}^{-2} \text{ s}^{-1}$ for the other fluences. The optical transmission (T) of the samples was investigated by using a halogen lamp and a TRIAX320 monochromator equipped with a Symphony CCD camera (Jobin Yvon), in the range 400–800 nm, with the exception of the pristine PC measured from 350 nm to 800 nm. The UV–visible extinction spectra were obtained from the transmission measurements, as $\ln(1/T)$. The electrical resistance of the pristine as well as the implanted polymers was evaluated from current–voltage (I–V) characteristics. Silver paint drops were deposited on the corners of the squared samples to form the four contacts suitable in Van der Pauw configuration. Measurements were carried out at room temperature by means of a Keithley 4200 SCS analyser system equipped with four source–monitor units.

3. Results and discussion

The extinction spectra of the samples implanted with 1 MeV non-metal ($^4\text{He}^+$, $^{12}\text{C}^+$) and metal ($^{63}\text{Cu}^+$, $^{107}\text{Ag}^+$, $^{197}\text{Au}^+$) ions are reported in Fig. 1a and b, respectively. In both graphs the spectrum measured for a pristine PC matrix is also shown for comparison. Irrespective of the ion species, some common characteristics can be highlighted in the spectra. In the entire spectral range analyzed, the extinction increases with the fluence showing a more marked rise in the close UV region, that can be related to the formation of a conjugated bond domain resulting from the defects produced upon the irradiation [14]. Whilst for fluences below $\leq 1 \times 10^{14}$ ions cm^{-2} only a weak absorption tail is observed, two main features can be identified in the whole set of spectra evolving as a function of the ion fluence, irrespective of the ion species. A band between 450 nm and 460 nm appears for fluences $\geq 6 \times 10^{13}$ ions cm^{-2} and a band at 580 nm for fluences $\geq 7 \times 10^{15}$ ions cm^{-2} . An additional band between 510 nm and 520 nm appears for fluences $\geq 1 \times 10^{15}$ ions cm^{-2} but only for metals (neither for He at 2×10^{15} ions cm^{-2} , nor for C at 7×10^{15} ions cm^{-2}). These

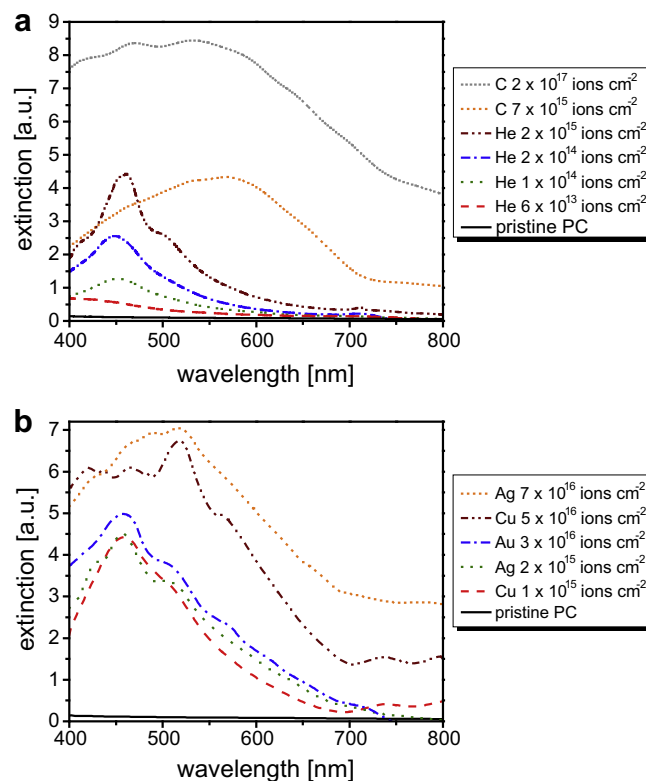


Fig. 1. Extinction spectra of PC matrices implanted with 1 MeV non-metal (a) and metal ions (b) with fluences as labeled close to each graph. For comparison are also reported the spectra of the unimplanted PC.

absorption bands can be only related to modification induced inside the polymer by the implantation process and reveal the presence of C_{x0} clusters and/or C_{x0} cluster aggregates [15,16]. It is worth nothing that for $^{63}\text{Cu}^+$ implanted samples, the band between 450 nm and 460 nm is more intense with respect to other species, as can be observed for $^4\text{He}^+$ and $^{107}\text{Ag}^+$ sample implanted with 2×10^{15} ions cm^{-2} with respect to $^{63}\text{Cu}^+$ 1×10^{15} ions cm^{-2} . These results point out that other factors comes into play in defining the absorption behavior at these wavelengths when $^{63}\text{Cu}^+$ ions are implanted in PC, one possibility being the contribution of the two 1 s excitonic transitions of copper oxide, Cu_2O , nanoparticles (NPs). Indeed, as already reported in our previous work [10], when metal ions are surrounded by an oxygen rich matrix the formation of oxides is expected, irrespective of the synthesis technique [17].

For metal implanted specimens additional bands can be detected, evolving in intensity and redshifting as the ion fluence increases. Whilst, for $^{63}\text{Cu}^+$ samples an absorption band at 550–570 nm is found, for $^{107}\text{Ag}^+$ the additional band is at 470–490 nm and for $^{197}\text{Au}^+$ at 515–570 nm. All these structures can be explained by considering the Surface Plasmon Resonance (SPR) associated to the collective oscillation of free electrons in metal NPs [18]. As reported elsewhere, a fraction of the implanted ions is still in atomic state and, then, not involved in the formation of metal and/or metal–oxide aggregates, as it is indirectly confirmed by the background signal intensity in the extinction spectra [1,10].

The increase of the extinction, irrespective of the ion species is accompanied by the shift of the absorption edge towards the visible region, both behaviors being solely related to modification of the polymer matrix because, as a matter of fact, they only depend on the ion fluence and then on the bonds scission and formation of extended systems of conjugated bonds [4,19,20]. The reduction of

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