Structural and electrical transformations in Ag-implanted polyethylene terephthalate (PET) induced by swift heavy ion irradiation

Jean J Mboukam[1], Daniel C Chilukusha[1,3], Morgan Madhuku[2] and Mandla Msimanga[1,2]

[1]Photovoltaic NanoComposites R and D Platform Physics Department, Tshwane University of Technology P Bag X680, Pretoria 0001, South Africa
[2]iThemba LABS, Tandem and Accelerator Mass Spectrometry Department, P. Bag 11, Wits 2050, South Africa
[3]Department of Physics, Mulungushi University, Kabwe, 10101, Zambia

E-mail: jules.mboukam@gmail.com

Abstract. The present study investigates the combined effects of ion implantation and swift heavy ion irradiation on the structural and electrical properties of polyethylene terephthalate (PET). Samples were first implanted with 150 keV Ag^{+}-ions at fluence of 1×10^{17} ions/cm^2 then irradiated with 30 MeV Au^{7+}-ions. Atomic force microscopy (AFM) images and optical micrographs reveal blistering induced by swift heavy ions, especially for the implanted sample. Raman studies show two bands with the larger band indicating the presence of amorphous and graphite-like structures in the samples. The band intensities decrease depending on the processing conditions, signifying optical and structural transformations in the implanted and/or irradiated PET. Current-voltage (I-V) measurements indicate an increase in the conductivity of the implanted samples, which is further enhanced upon irradiation, highlighting a transition from insulating to semiconducting behavior.

1. Introduction

The exceptional mechanical, chemical, and thermal properties of polyethylene terephthalate (PET) make it a popular polymer in various industrial and scientific applications [1, 2]. However, its application in advanced electronics and optoelectronics is hampered by its electrically insulating characteristics. A successful method for altering these characteristics is ion implantation followed by swift heavy ion (SHI) irradiation [3, 4]. While additional SHI irradiation causes structural changes such as carbonisation, defect formation, and the production of nanoclusters, the addition of silver (Ag) ions into PET can generate conductive pathways [3, 4]. Silver is one of the noble metals that has been widely employed for generating nanoparticles within polymer matrices due to its propensity to nucleate and aggregate at high fluence [3]. A number of variables, including ion fluence, energy, and the characteristics of the polymer, affect the size and dispersion of these nanoparticles and make them conductive [3]. The electrical conductivity of the polymer can be considerably changed through the disruption from electronic excitations and sputtering processes due to high energy deposition during irradiation [5, 6],

which makes it appropriate for use in sensors and flexible electronic devices, such as optical waveguides, picosecond optical switches, and other nano- and optoelectronic devices [4, 7].

This work, therefore, examines the synergistic effects of 150 keV Ag^{+}-ions implantation and 30 MeV Au^{7+}-ions swift heavy ion irradiation on the structural and the electrical characteristics of PET.

2. Experimental Details

Commercial foil of PET ($C_{10}H_8O_4$) with a thickness of 130 μm was purchased from Sigma-Aldrich and cut in pieces of 12 mm $\times$ 12 mm. This was followed by the cleaning steps in chemical solutions of ethanol and acetone using an ultrasonic bath as in Ref [4]. Following preparation, the samples were implanted with 150 keV Ag^{+}-ions using a Varian-Extrion implanter (model 200-20A2F). A low current of 0.40 µA was used during the process at liquid nitrogen temperature in order to limit sample damage from beam-induced heating [8]. The range of the silver particles into the PET matrix was determined to be about 102 nm [9] using the Stopping and Range of Ions in Matter (SRIM/TRIM) simulation code [10]. Pristine and Ag^{+}-ions implanted PET samples were irradiated with 30 Au^{7+}-ions at a fluence of 2×10^{13} ions/cm^2 using a 6 MV Tandem Accelerator under high vacuum (10^{-6} mbar). Raman spectroscopy was performed using a WITec alpha 300 RAS^{+} confocal micro-Raman microscope with a 532 nm laser source. The system's integrated platform was also employed to perform atomic force microscopy (AFM) and optical imaging of the samples. Current-voltage measurements were conducted using a Keithley 2450 source-meter unit by sweeping the voltage from -3 V to +3 V. Figure 1 below displays the schematic representation of the I-V device used for electrical investigations.

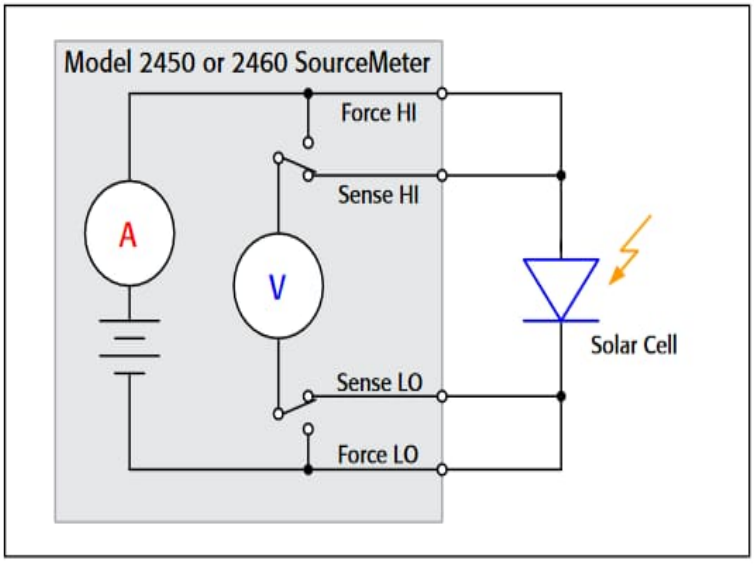

Figure 1: Schematic diagram of the electrical characterisation device.

3. Results and discussion

3.1. Structural Analyses:AFM

Atomic Force Microscopy (AFM) and optical micrographs provide valuable information about the surface morphology and topographical features of the implanted/irradiated PET. Figure 2 (top images) depicts the surface topography of the samples: Ag^{+}-implanted (left), pristine irradiated with 30 MeV Au^{7+}-ions (middle), and Ag^{+}-implanted followed by Au ion irradiation

(right). The surface morphology of the implanted PET at 1×10^{17} ions/cm^2 initially shows a smooth texture. However, it drastically increases in surface roughness upon implantation and subsequent irradiation, leading to the formation of conductive carbon clusters at the near surface of the thin film, supported by UV-Vis studies [7]. The images also provide evidence of blistering induced by swift heavy ion irradiation, which is more pronounced for the implanted and irradiated sample. In the micrographs (bottom images), one can observe changes in surface contrast and texture, particularly in the implanted and irradiated samples, suggesting structural or compositional alterations near the surface, implying the formation of conductive carbon clusters at the near surface of the samples.

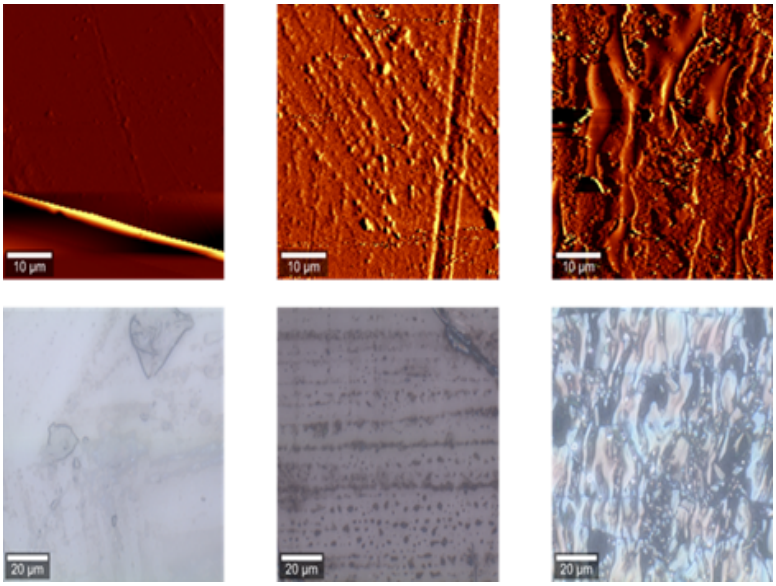

Figure 2: The top panel shows AFM images of PET films: implanted with 150 KeV Ag^+ ions (left), irradiated with 30 MeV Au ions (middle), and implanted-irradiated (right). The bottom panel presents corresponding optical micrographs.

3.2. Structural Analyses:Raman Spectroscopy

The progressive structural changes in the implanted and irradiated PET have been seen on Raman spectra as observed in figure 3. The peaks observed on the pristine spectrum at 857, 1286, 1613, and 1723 cm^{-1} are assigned to the C–C breathing (ring and complex O-C stretching mode), ring C = C stretching, and C=O stretching modes [4], respectively. The energy deposition from implantation and irradiation causes these peaks to reduce and even disappear, as observed in the implanted and/or irradiated spectra (see red, blue and pink spectra), suggesting the structural modification of the polymers. Figure 3 shows the structural modification of the polymers through implantation and irradiation processes with D and G bands formed at 1345 and 1583 cm^{-1}. Due to nuclear stopping and electronics processes, which are both frequently in charge of the intense degassing of the irradiated PET and the subsequent carbonisation of the near-surface layer of polymers, these bands are indicative of graphite-like structures originating from sp^2 hybridised C atoms [4]. While the D band identifies breathing modes specific to rings, the G band denotes stretched modes shared by both rings and chains [4]. It has been noted that the centroid of the G band (1582 cm^{-1}) precisely corresponds to the one of pure graphite/graphene. The ratio of D and G peaks (I_D/I_G) can be used to determine the well-organised carbon structures or damage that have typically been produced from rings as a result of implantation and radiation-induced by heavy ions. The calculated ratios were obtained to be 0.25, 0.87 and 0.95 for the

irradiated PET and irradiated/implanted samples. The obtained ratio values are higher than those reported for Si-ion irradiation [4], confirming that the the degree of damage depends on the ion type and ion fluence. The increase of this factor confirms the gradual modification of the polymer matrix. On the other hand, the enhanced contrast, manifested as increased variation in light and dark regions on the optical micrograph images confirm the structural changes in the samples during implantation and/or irradiation and corroborate with the AFM results.

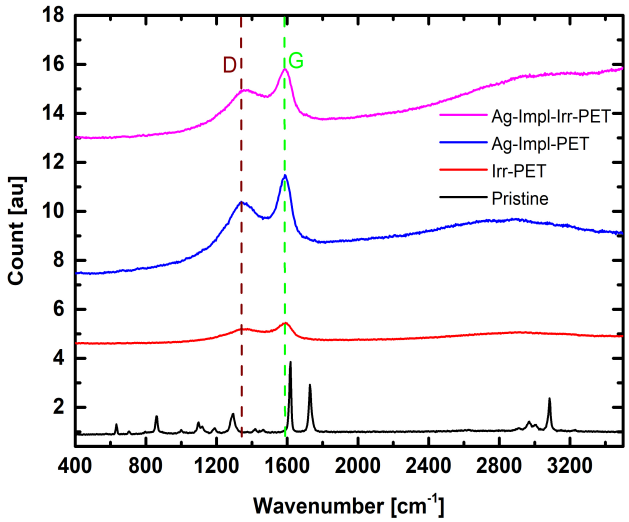

Figure 3: Raman spectra for pristine (black curve) and PET irradiated (red) and Ag-implanted and irradiated PET to 1×10^{17} ions/cm^2 (blue and pink), respectively.

3.3. Electrical characterisation

Figure 4 presents the I-V characteristics of pristine irradiated PET, Ag-implanted PET, and Ag-implanted PET further irradiated with 30 MeV Au^{7+}-ions. The pristine irradiated sample (blue curve) exhibits negligible current response across the entire ±3 V range, consistent with its insulating nature. In contrast, the Ag-implanted sample (orange curve) shows a moderate increase in conductivity, attributed to the formation of defect sites and partial clustering of silver within the PET matrix [4, 7]. The highest conductivity is observed in the Ag-implanted and Au-irradiated sample (green curve), which exhibits a nearly linear and symmetric IV profile, indicating enhanced charge transport pathways. This improvement is likely due to the formation of conductive Ag nanoclusters and carbonaceous structures induced by the combined effects of implantation and swift heavy ion irradiation.

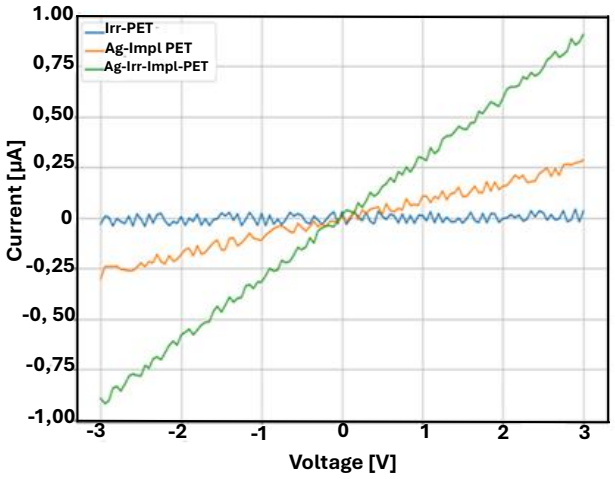

Figure 4: Voltage dependencies of electric current for samples implanted with 150 keV and further irradiated with 30 MeV Au^{7+}-ions.

4. Summary

Pristine and Ag-implanted PET at fluence of 1×10^{17} ions/cm^2 with 150 keV and further irradiated with 30 MeV Au^{7+}-ions have been investigated. The first observation was the yellowing and darkening of the transparent PET after implantation and/or irradiation. The colouration was attributed to the breaking and formation of conjugated bonds, as observed in the structural molecular studies. It has been observed that Ag-implanted PET undergoes notable structural and electrical changes due to the swift heavy ion radiation. Changes in morphology and structure increased electrical conductivity, which indicates that the irradiation process causes the polymer matrix to reorganise, nanoparticles to aggregate, and conductive pathways to develop. These changes are highly reliant on the ion fluence, suggesting that the material properties can be modified. The findings show how ion beam techniques can be used to develop polymer-based nanocomposites with specific structural and electrical properties for cutting-edge technological applications.

Acknowledgments

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