

**CRYOGENIC ION IMPLANTATION OF POLYETHYLENE
TEREPHTHALATE (PET) THIN FILMS: STRUCTURAL AND
ELECTRICAL PROPERTIES**

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GAOPALELWE MOTAUNG

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Supervisor: Prof. S. J. Moloi

Co-supervisor: Prof. M. Msimanga

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DECLARATION

Name: GAOPALELWE MOTAUNG

Student number: 62700030

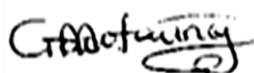
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TEREPHTHALATE (PET) THIN FILMS: STRUCTURAL AND ELECTRICAL
PROPERTIES

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ACKNOWLEDGEMENTS

The journey to completing this dissertation has been an incredibly difficult one, but with adversity one needs a spirit of resilience and surely there will be light at the end of the tunnel.

I would like to thank my co-supervisor, Professor Msimanga of the Tshwane University of Technology, for his patience and commitment throughout my journey, most of all I am grateful for his tireless spirit and passion for teaching since my undergrad years. Thank you Professor Moloi, my supervisor, for your endurance and always making sure that everything is running smoothly academically. To my family; thank you for the love, you have carried me and this wouldn't have been possible without your support. My dad, mom and sister, Moeketsi, Gaelebale and Lerato Motaung, I love you and I truly am blessed. To my friends, thank you for the advice and encouragement in the past years; you are the best and are all appreciated.

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Not forgetting the Lord our God for guidance, strength and faithfulness. Your grace kept me afloat.

Keywords: Polyethylene terephthalate (PET), ion implantation, surface modification, carbonisation, structural properties, optical properties, electrical properties, depth profiling.

DEDICATION

I would like to dedicate this dissertation to my niece, Gofaone, my two nephews, Ogodiseng and Oboitshepho. You all bring joy into my life. I pray that you grow up to be the best versions of yourselves and experience less of this worlds tragedies. I love you.

ABSTRACT

Conventional inorganic semiconductors such as silicon, germanium and gallium arsenide have been the backbone of the semiconductor industry over the past few decades. In recent years, organic electronics have attracted attention in the semiconductor industry for many different applications which include photovoltaic cells, light emitting diodes, transistors and so on. The development of organic electronics stems from the improvement of the properties of polymers through various fabrication methods, one such method is ion implantation. Ion implantation offers an effective solution in modifying surface properties of polymers such as hardness and wear resistance, physical and chemical properties are also altered. These include: cross linking which enhances the conductivity of the implanted material, chain scission and carbonization. Ion implantation of polymers have some advantages over other fabrication methods, these methods include: chemical synthesis, vacuum deposition, plasma polymerization, and etc. Low filling factor and a large dispersion in sizes and shapes of nanoparticles are a few of the problems these methods pose. Ion implantation enables a high metal filling factor to be reached in a solid matrix. Polyethylene terephthalate (PET) is a very common and readily available polymer in the plastics industry. Since PET is a naturally insulating material, the possibility of modifying its conductance opens up a range of possible applications for this polymer in the semiconductor industry.

In this work samples of PET films were implanted at liquid nitrogen to various fluences using 100 keV argon and titanium ions with the objective to characterise its properties using different material characterization techniques. The samples were cleaned through a process of inserting them in beakers of small amounts of acetone, ethanol and distilled water respectively at two minute intervals, they were dried by using nitrogen gas.

The chemical structure of the films was investigated using x-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy; the semi-crystalline structure exhibit properties that

indicate that they have undergone degradation with breakage and destruction of some bonds. The morphology, via scanning electron microscopy (SEM), show formation of granular materials. Depth profiles acquired by using heavy-ion elastic recoil detection analysis (HI-ERDA) show an accumulation in carbonization in the films with increase in fluence; a decline in the carbon content is observed in depths where there is accumulation of the implanted species. The ultraviolet-visible (UV-Vis) spectroscopy results show a redshift in the spectra with a decrease in the optical energy band gap from 3.55 eV for the pristine to 2.01 and 1.84 eV for argon and titanium respectively for samples implanted at the highest fluence. This is accompanied by increases in the activation energy and number of carbon cluster. The electrical structure of the films has been modified, with current-voltage (I-V) results showing a decrease in the surface resistivity and increase in the current. The characteristic measurements show that there is an overall increase in carbonization and formation of carbon clusters thereby enhancing the electrical properties of PET.

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CHAPTER 1: INTRODUCTION

1.1 Background and literature review

Polyethylene Terephthalate is a naturally transparent and semi-crystalline polymer and is one of the most common and widely used polymers in the world. Abbreviated PET or PETE [1, 2], this polyester thermoplastic polymer resin is used in the food and beverage packaging industry (referred to as PET) and for fibre production (referred to as polyester) since its development in the 1940's [2, 3, 4]. In the past few decades PET has attracted considerable attention in the production of photonic and electronic devices due to the combination of its unique characteristics which include its chemical, electrical, mechanical, structural and optical properties (see Table 2-1 for properties of PET) and relatively low cost of production [5]. Since PET is a polymer; and therefore a naturally insulating material, the need to improve its electrical properties through modification of its conductance is a focal research area in the semiconductor industry. Through ion implantation, surface and/or bulk properties of polymers can be modified by control of the distribution of implanted species by altering the implantation parameters such as energy, current, type and fluence of ion [6].

Polyethylene terephthalate is often used to replace metals in sensors, switches, capacitors, light emitting diodes, photovoltaic cells and other electrical applications [7]. Previous research has shown that the electrical properties of PET can be modified through ion implantation [8, 9]. PET is colourless, strong, lightweight and transparent before implantation. After implantation the colour changes into a light brown at a dose of $\sim 10^{15} \text{ cm}^{-2}$. The transparent surface becomes opaque for doses higher than $\sim 10^{16} \text{ cm}^{-2}$ and thus the film changes into a dark brown. A metallic bright PET is produced when over $\sim 10^{17} \text{ cm}^{-2}$ ions are implanted [10, 11]. These effects are due to the

fact that accumulation of carbon clusters and the precipitation of metal ions is taking place during implantation due to polymer degradation, this also means that the higher the ion fluences, the darker the film will be; therefore, the electrical conductivity of PET is enhanced [5]. Since polymers are electrically insulating materials with conductivity values as low as $10^{-7} - 10^{-14} \text{ S cm}^{-1}$ [12], the conductance can rise by up to 10-15 orders of magnitude, with an increase in fluence, reaching the level of poor conductors, depending on the polymer type and implantation regime [6, 8]. High fluence implantation induces damage and by varying the ion energy, fluence and current it is possible to tailor the nature of the damages [13].

Ion implantation is a powerful and versatile tool for modification of polymers [6]; this method offers very precise control of the distribution of the implanted dopants by altering the implantation parameters [12]. Control of the ion implantation energy, fluence and ion species is a key point for the obtaining of materials with required parameters [6]. This technique is very effective for improving surface properties of polymers without altering their bulk properties [8, 12]. Bombardment by energetic ions induces a variety of processes in the subsurface layer resulting in modification of its physical and chemical properties. These include: bond breaking, cross-linking, polymer chain scissions, gas release and carbonisation [12].

Effects of ion implantation on structure and composition of polymers is a complex phenomenon. Physical and chemical processes depend on the implantation energy and mechanisms of energy transfer as well as on the composition and structure of a pristine polymer [6, 9]. There is loss of energy when an ion penetrates a material until it comes to rest in the material. Energy losses are due to elastic and inelastic collisions. When an ion has lost all its energy and comes to rest in the substrate, it is said to be implanted in the material. The factor that determines that final distribution of ions and defects is the energy loss by ions in a material. An energetic ion penetrating a material loses energy mainly via two processes which are considered to be independent of each other [14].

They are: elastic nuclear collisions and inelastic electronic interactions. Both mechanisms act simultaneously during surface impact and further ion movement in the target depending on energy of the energetic particles [6, 8]. Energy loss of the projectile is characterised by nuclear and electronic stopping power, S_n and S_e , respectively. The nuclear stopping power dominates at low energies, while electronic stopping power dominates at higher energies [14]. The process of nuclear stopping includes all the processes that result in the transfer of energy (energy transfer leads to bond breakage [6]) from the implanted ion to the target atom as a whole. Electronic stopping is the process where an energetic ion penetrating a material loses its energy to the target electrons [14]. Energy deposition by means of electronic stopping results in excitation of polymer units [8].

Electrical conductivity in a composite is explained by the Theory of Percolation and Percolation Threshold [15]. The percolation threshold is the point where there is enough metal filler in the composite to start forming conductive networks, these networks form a continuous path that allows electricity to pass through a composite, thus increasing the electrical conductivity [12]. There are three states of electrical conductivity. Firstly, at low filler concentrations, filler particles act like conductive islands in the sea of electrically insulating polymer matrix. On further introduction of fillers, the conductive particles become more crowded and are more likely to come in contact with each other. And finally, at a critical volume concentration (percolation threshold), most of the filler particles get in contact with their neighbouring particles, thereby forming continuous network. Electrical charge can now flow without encountering high resistance of the polymer. After the percolation threshold has been reached, the electrical conductivity will flatten and approach the electrical conductivity of the filler used in the composite [12].

The formation of conductive paths is also described by a decrease in resistance which is caused by the growing concentration of conjugated double bonds and production of carbonaceous clusters at

high ion fluences [9, 16]. High fluence ion implantation leads to several phenomena that may change electrical properties of the polymer significantly. Increasing ion fluence, nanoparticles cluster, and polymer composition changes due to ion irradiation, which leads to carbonization of the surface layer, are some of the important changes that influence the conductivity/resistivity of the implanted sample [9].

While polymer-based electronics have had considerable progress in the past few decades, modification of electrical properties of polymeric materials through ion implantation is not as well studied as that of inorganic semiconductor materials. There could be possible future applications for organic electronics beyond current uses in display, lighting and organic solar cells, and there continues to be a need to develop and improve the efficiency, performance and operating life-time of these devices. In radiation detection or harvesting for instance, inorganic semiconductor materials dominate the field. To introduce inexpensive, polymer-based devices in this field, extensive research in organic materials modification has to be conducted in order to achieve desired the properties; such as increasing charge-carrier mobility and improving quantum efficiency of polymeric radiation detectors.

One of the ion beam-induced changes in polymers during ion implantation is loss of molecular fragments through sputtering brought about by poor thermal energy dissipation within the polymer. This has a detrimental effect on the structural integrity of the polymer, especially if it is a thin film, and should be avoided or minimised where possible. The aim of this project therefore was to perform ion implantation of PET at cryogenic temperature, and carry out a systematic study of the changes in the structural and electrical properties of PET foils implanted with metallic and non-metallic ions at this low temperature. The work formed part of a broader study aimed at developing polymer-based nanocomposites for applications in nuclear and solar radiation sensor devices.

1.2 Problem statement

Since the discovery of electrically conductive polymers in the 1970's [17], a lot of research has been conducted with hopes of developing polymer nanocomposites that are efficient solar radiation harvesters and have high performance. Ion implantation research has been done using different combinations of ion species and target polymers, implantation energies, current densities and fluences. Although extensive research has been conducted on PET, most of the ion implantations performed on the polymer and reported in literature have been done under room temperature conditions [2, 9]. Not much has been done to investigate the effects of the temperature of the target material during implantation, on the final electrical and optical properties of the PET polymer. This work was based on the postulation that ion implantation at cryogenic (e.g. liquid nitrogen) temperatures might alter the defect growth mechanism from what is currently known and understood. This could lead to realisation of previously unobserved properties in the implanted PET films.

1.3 Research aim and objectives

1.3.1 Aim

The aim of this work was to investigate structural changes and electrical properties of ion implanted PET thin films using different analytical techniques, with a broader aim of improving properties of PET for various electronic and optoelectronic applications. In achieving this aim, metal and non-metal ions were used to implant the thin films at cryogenic temperatures so as to compare the behaviour and changes in the properties of the polymer after implantations.

1.3.2 Objectives

In pursuit of this aim, the following objectives were set:

1. Material preparation

This process was carried out at iThemba LABS (TAMS). Preparations of the material included implantation of PET films at different fluencies (2×10^{16} , 8×10^{16} , 1×10^{17} , 1.4×10^{17} and 2×10^{17} ions/cm²) using 100 keV Ti⁺ and Ar⁺ ions. The implantations were done at liquid nitrogen temperature.

2. Material characterization

Structural characterization of ion implanted PET films were carried out using the following techniques:

- X-ray Diffraction Spectroscopy (XRD) to determine the crystallinity of the PET thin film
- Scanning Electron Microscopy (SEM) to determine the morphology of the implanted PET
- Elastic Recoil Detection Analysis (ERDA) to determine depth profile of the implanted species
- Fourier-Transform Infrared spectroscopy (FTIR) to determine any changes in the chemical and molecular structure of the PET
- Ultraviolet-Visible spectroscopy (UV-Vis) to determine any changes in the electronic band gap of the PET

3. Device characterization

Electrical characterization of ion implanted PET films was carried out using the following techniques:

- (Current-Voltage) I-V characteristics

1.4 Dissertation outline

The dissertation outline is as follows:

- Chapter two begins with a description of polyethylene and its properties, and goes on to describe briefly how it is manufactured. This is followed by a discussion of the interactions and material effects of different types of radiation quanta and light particles on polyethylene. The end section of the chapter details the interaction and effects of charged particles, such as ions from an ion implanter, on properties of polyethylene.
- Chapter three outlines the preparation of PET samples, the experimental procedures and techniques which are used for the characterization of virgin and implanted PET samples. Characterization techniques will provide information about the material structure, morphology, depth profiles of the implanted species and the electrical properties of the material before and after ion implantation.
- The results obtained from each characterization technique listed/mentioned in chapter three are provided in chapter four, accompanied by a discussion of each result.
- Chapter five gives a brief summary of the entire dissertation and it is as well a conclusion to the work provided.

CHAPTER 2: THEORETICAL OVERVIEW

2.1 Introduction

External factors, such as oxidation, fatigue, friction, wear etc. may cause damage to the surface of materials. Since the surface layer is the first part of a material that interacts with the external environment, it is therefore imperative to enhance the physical and chemical structure of materials to achieve desired properties and also to prevent surface damage. Photon radiation and nuclear particles like alphas and neutrons interact differently with matter and have been used in certain instances to modify surface properties of polymeric materials [18, 19]. Using energetic ion beams from particle accelerators, the surface layer of materials is bombarded with ions and, depending on the energy and thickness of the material, the ions may pass through or get embedded in the material [20]. The latter, which is introduction of foreign atomic species into the target material is generally referred to as the ion implantation technique. This non-equilibrium method of modifying solids is independent of thermodynamic factors [20, 21]. This chapter describes physical properties of PET and how these properties can be modified by different forms of radiation.

2.2 Properties and synthesis of PET

Polyethylene terephthalate (PET) is a condensation polymer produced by the trans-esterification or esterification of ethylene glycol (EG) with either dimethyl terephthalate (DMT) or terephthalic acid (TPA) respectively [22, 23]. This polyester thermoplastic has a semi-crystalline nature (see Figure 2-2) and it consists of polymerized units of monomer ethylene terephthalate with a chemical formula $C_{10}H_8O_4$ [24], the repeating unit for PET is shown in Figure 2-1.

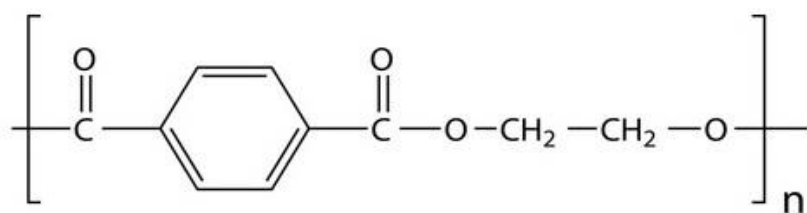


Figure 2-1: Repeating PET unit [22].

The degree of polymerization (DP) is the main factor that determines the properties of PET. The DP is characterized by the amount of viscosity of the polymer [22, 25, 26]. Generally, lower intrinsic viscosity PET (<0.75 dL/g – decilitres per gram) is used in applications such as food packaging, photographic films and apparel fibres. Higher intrinsic viscosity PET (>0.9 dL/g) is usually used in “heavy-duty” applications. High- and low- viscosity PET can be produced by both DMT and TPA processes [25].

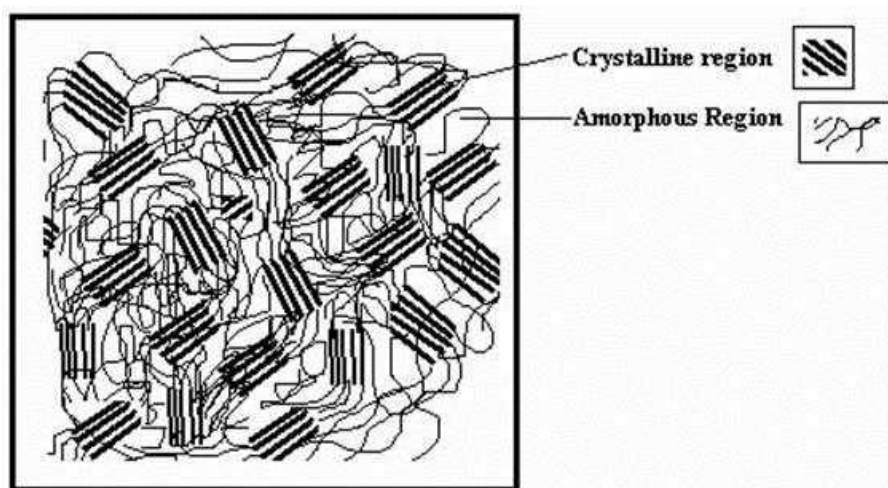


Figure 2-2: Mixed amorphous crystalline (semi-crystalline) macromolecular polymer structure [24].

Table 2-1: Properties of PET [27, 28, 29]

Properties	
Crystalline structure	Amorphous and semi-crystalline
Density	1.35 - 1.41 g/cm ³
Molecular weight (per repeating unit)	192 g/mol
Melting temperature	260 °C
Glass transition temperature	67 – 81 °C
Thermal conductivity	0.15 - 0.24 W/mK
Elongation at break	30 – 300 %
Yield strain	4 %
Young's Modulus	2800 - 4100 MPa
Tensile strength	48 – 72 MPa
Impact strength	90 J/m
Volume resistivity	> 10 ¹³ ohm.cm
Dielectric strength	5.0 V/mm x 10 ⁴

2.2.1 PET synthesis

Production of PET involves four main stages; 1) trans-esterification/esterification, 2) pre-polymerization, 3) melt polycondensation and finally 4) solid state polycondensation [30]. The different stages in the production of PET are depicted in Figure 2-3.

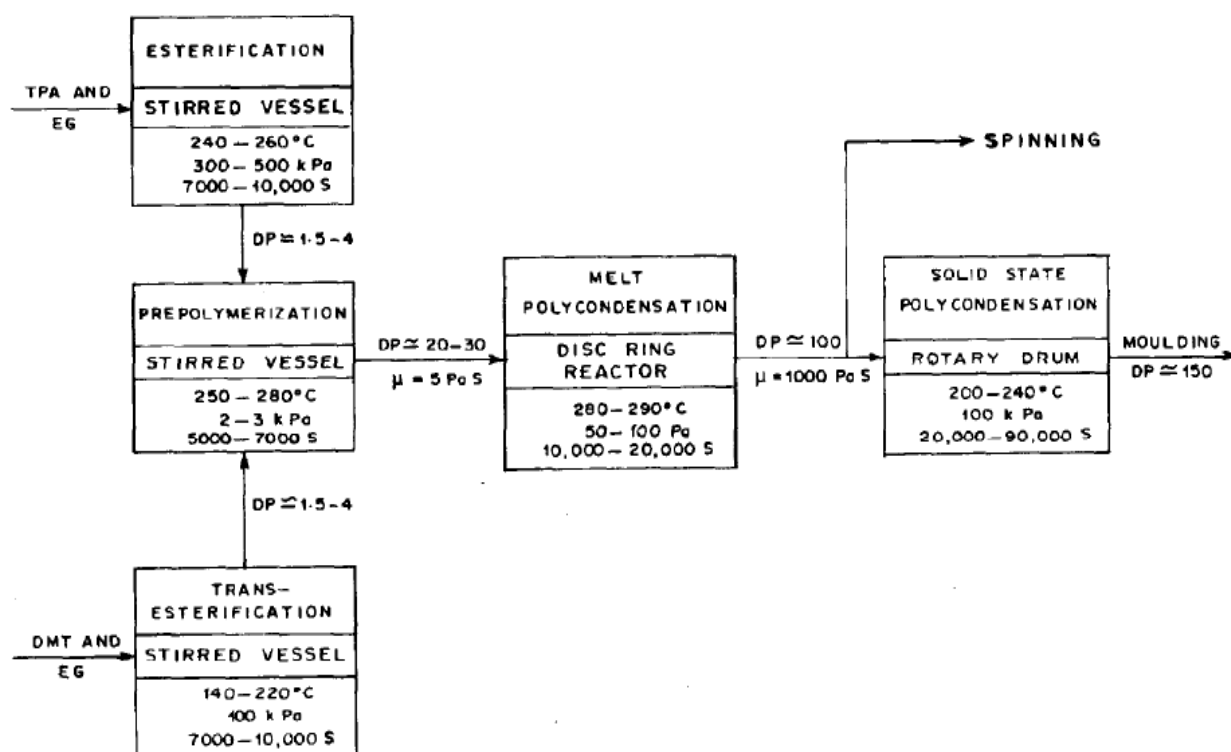


Figure 2-3: Different stages to PET synthesis [30].

Due to the fact that DMT could produce the ester at a purer form than the TPA, it was a preferred method of synthesising the polymer until the mid-1960's [31]. TPA gained popularity after the development of high-purity terephthalic acid processes and is now the preferred process. The need to recover or recycle methanol is eliminated by the use of high purity TPA (purified terephthalic acid – PTA) [22, 25].

The synthesis of PET takes place in the following steps: [22, 26, 30]

1. **Trans-esterification by dimethyl terephthalate (DMT):** Ethylene glycol (from a raw material storage) is mixed with additives and catalysts; the mixture, along with DMT is then transported to esterifiers/ester reactor (not shown in Figure 2-3). Each pound (1 lb = 0.4536 kg) of PET can be obtained from 0.6 lb of EG and 1.0 lb of DMT. The trans-esterification reaction then takes place at 140 - 230°C and 100 kPa. Bis-hydroxyethyl

terephthalate (bis-HET/BHET) becomes the output of the reaction along methanol; methanol is continuously removed from the esterifiers and sent to storage.

Esterification by Purified Terephthalic acid (PTA): In the direct esterification process TPA is reacted with EG and the byproduct, water, is removed. The removal of water rather than methanol simplifies the recovery facilities. The reaction times are shorter as the reaction operates at temperatures greater (240 – 260 °C) than the normal boiling point of glycol and pressures greater (300 – 500 kPa) than the atmospheric pressure.

2. In the pre-polymerization reactor, BHET with some oligomers (polymers with few repeating units) is polymerized ($DP = \pm 30$) at 250 – 280 °C and 2 - 3 kPa; then the PET production reaction begins.
3. Products from the pre-polymerization reactor are fed through the melt polycondensation where further polymerization ($DP = \pm 100$) occurs at 280 – 290 °C and high vacuum/low pressure. At this point, the viscosity of PET is determined by the final temperature and pressure. The polymer melt is sent to spinning and produces PET that can be used for fibre and sheet applications.
4. The solid state polycondensation (SSP) stage occur when there is a need to produce PET (moulding grade) with high molecular weight (MW) and high viscosity (η). In order to produce high MW PET, chips are made from melt that is acquired from the melt polycondensation stage is solidified; these chips are then transferred to SSP. In this case the DP is increased to > 150 and the operating conditions are 200 – 240 °C at 100 kPa.

2.3 Radiation induced modification on material properties

The transmission or emission of energy that travels through a medium or space is known as radiation; which comes in the form of particles (alpha, beta, neutrons, X-rays and gamma rays) or

waves (electromagnetic waves such as ultraviolet, microwaves, radio waves etc.). Figure 2-4 shows a diagram of the electromagnetic spectrum. There can either be ionizing or non-ionizing radiation, this is dependent upon the amount of energy the particle/wave has. Ionizing radiations have energies that are greater than 10 keV, this energy is enough to ionize atoms and cause chemical bond breakage [32]. The emission of radiation originating from a nuclear reaction or spontaneous decay of unstable atomic nuclei is known as radioactivity. Energy losses due to the emission of elemental particles cause an unstable atomic nucleus to decay directly from the nucleus or the electron shells. The amount of a radionuclide is directly proportional to the decay/disintegration rate of that specific radionuclide [33]. Different types of radiation will have different effects on materials due to different interaction mechanisms. A closer look at the different radiation types and their effects on material follows below.

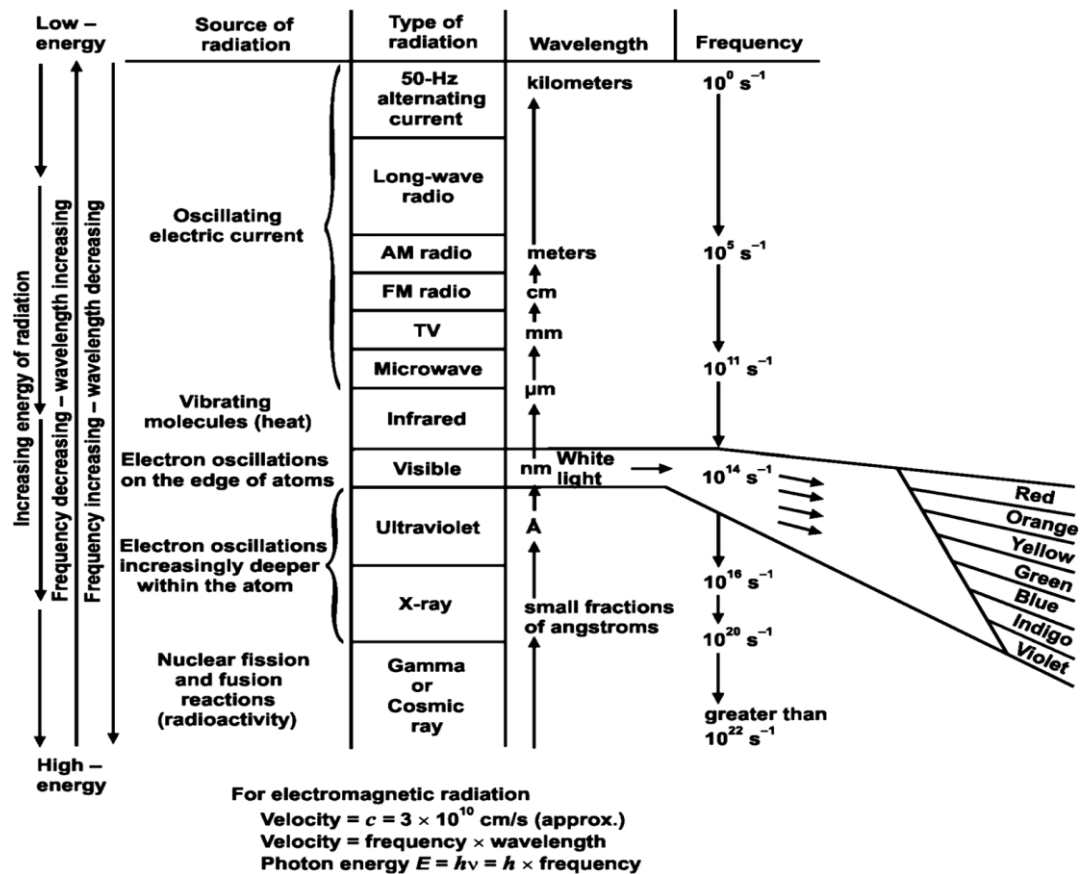


Figure 2-4: Electromagnetic spectrum [33].

It is fundamental to understand the interaction of different types of radiation with matter because the detection of radiation is based on this concept and how the energy of these radiations dissipates in the material in which the detector is made of. This can therefore help when designing radiation detectors. The three types of ionizing radiation are as follows:

1. Charged particles: electrons, positrons, protons, deuterons, alphas and heavy ions ($A > 4$)

Charged particles lose their energy in matter through:

- a. Coulomb interactions
- b. Bremsstrahlung emission
- c. Cerenkov emission
- d. Nuclear interactions

2. Photons: gamma rays and X-rays

3. Neutrons

Distinguishing the radiations into groups makes it easier as each has its own characteristic properties. The properties are discussed in the below sections (2.3.1 – 2.3.5).

2.3.1 Alpha radiation interaction effects on matter

A nuclear decay process where an alpha (α) particle is emitted from a parent nucleus is called alpha decay. An alpha particle consists of two protons and two neutrons therefore it is structurally equivalent to a nucleus that of a helium atom [33]. An alpha particle has a charge of +2 and a mass of 4u. When an alpha particles decays, it transforms into a different atomic nucleus where the mass number is reduced by four and the atomic number is reduced by two [32]. Alpha particles are mostly emitted from radionuclide of atomic number greater than 83 [33].

Coulombic interactions occur between traversing alpha particles and orbital electrons of a particular atom; this is possible because α -particles have double positive charge (two protons and two neutrons) and electrons have a negative charge therefore ionization occurs as a result of the formation of ion pairs due a Coulombic attraction [34]. And since the mass of α -particle (4 amu) is much greater than that of an electron (5×10^{-4} amu); this also permits the ejection of electron from an atom. Due to the huge difference in mass between the two particles, along its path; the α -particle continues to experience negligible deflection as a result of the collision as well as the Coulomb interactions [33, 34, 35].

In very rare instances, the α -particle may interact with the atomic nucleus (positively charged) and scatter due to the Coulombic barrier. Incident particles have a higher probability of interacting

with electrons (radius of atom = 10^{-10} m) than they do with the nucleus (radius is approximately 10^{-14} m), therefore:

$$\frac{\text{Number of interactions with electrons}}{\text{Number of interactions with nuclei}} = \frac{(R)^2 \text{ atom}}{(R)^2 \text{ nucleus}} = \frac{(10^{-10})^2}{(10^{-14})^2} = 10^8 \quad (2-1)$$

Until all its kinetic energy is dissipated into the target material it is traveling in, the particle will continue creating ion pairs. For an alpha-particle traveling in air, it loses energy of 35eV for each ion pair produced; if it had energy of 5MeV then it would produce:

$$\frac{5 \times 10^6 \text{ eV}}{35 \text{ eV/ion pair}} = 1.4 \times 10^5 \text{ ion pairs} \quad (2-2)$$

Equation shows the number of ion pairs created by a 5 MeV α -particle traveling in air. The absorbing medium/target material is what determines the amount of energy required to produce an ion pair [33, 34].

Excitation of an electron will occur when an alpha-particle gives off sufficient energy to cause an electron to be completely ejected or rather for it to jump to a higher energy level. The electron will eventually return to a lower energy level giving off its energy as a photon [34, 35].

2.3.2 Beta radiation and effects on matter

Beta decay (β) is a type of nuclear decay process whereby the atomic number (Z) of a nucleus changes and the mass number (A) is constant. The three main types of beta decay process are as follows:

1. Negatron (β^-) emission is when a negative beta particle/electron is emitted from the nucleus.

2. Positron (β^+) emission is when a nucleus emits a positive beta particle or a positively charged electron.

3. Electron capture (EC) is when there is no beta particle emission [33, 34].

Both beta- and alpha-particles interact with matter via collisions resulting in electron excitation and ionization. Since the mass of a beta-particle is equal to that of an electron and also having a single charge; its lightweight allows it to travel faster (high velocity) than an alpha-particle having the same amount of energy. Due these characteristics, the ionization that the particle will produce in air is lower [34, 36].

Beta-particles get scattered from collisions because they have the same mass as electrons, this mass equivalence makes it possible for the β -particle to transfer most of its kinetic energy to the electron in a single collision and therefore leaving the particle with insufficient energy to cause further ionization. The ejected electrons (delta rays) will cause more ionization (secondary), which contribute about 80% of the total number on ionization produced [36, 37].

A third mechanism which is the dissipation of radiative energy via Bremsstrahlung (not mono-energetic radiation) emission/production making the total stopping power for beta-particles (β^+ or β^-) the sum of collisional and radiative contributions and is given by (Equation $\left(\frac{dE}{dx}\right)_{total}^{\pm} =$

$$\left(\frac{dE}{dx}\right)_{col}^{\pm} + \left(\frac{dE}{dx}\right)_{rad}^{\pm} \quad (2-3)$$

$$\left(\frac{dE}{dx}\right)_{total}^{\pm} = \left(\frac{dE}{dx}\right)_{col}^{\pm} + \left(\frac{dE}{dx}\right)_{rad}^{\pm} \quad (2-3)$$

where, the superscript $\pm$ represent a positively or negatively charged electron.

In absorbers with higher atomic number, Bremsstrahlung emission is associated with high energy β -particles. Bremsstrahlung photon energy can range from zero to that of the kinetic energy of the particle [38].

2.3.3 Neutron radiation and effects on matter

A neutron is a neutral particle that is found in the nucleus of an atom and it is only stable within the confines of that nucleus. The mass of a neutron is 1 u (atomic mass unit) which is equivalent to that of a proton and it also has a mean lifetime of about 15 minutes when it is outside the nucleus [34]. The emission of neutron radiation is not in any significant quantities from the radionuclide that undergo the traditional nuclear decay processes. Significant quantities of neutron radiation occur when neutrons are ejected from the nuclei of atoms following reaction between the nuclei and the particulate radiation. Since a neutron does not have a charge, it therefore cannot directly cause any ionization in matter [33].

Unlike charged particles, neutrons do not interact with matter via a Coulomb force which is the dominant mechanism for energy loss in charged particles. Neutrons only interact with the nucleus of an atom through nuclear forces and do not experience the Coulombic barrier [37]. Neutrons charge neutrality makes it possible for it to travel centimetres into the absorber without interaction. When interactions occur, the neutron may either be absorbed or captured by the nucleus which will result in the neutron losing its energy as a form of secondary radiation or the neutron can collide with the nucleus and get scattered in the process [33, 36, 37].

Secondary radiation can either be the emission of gamma radiation or heavy charged particles. Scattering of the neutron can be elastic (redistribution of the kinetic energy between the two particles) and inelastic (nucleus receives the kinetic energy as excitation energy) [38].

Elastic scattering: the interaction causes the scattering of the incident neutron and the recoil of the nucleus. The kinetic energy is conserved as the neutron gives off some of its original energy to the nucleus. This mechanism mainly occurs in fast neutrons when they interact with atomic

nuclei that have low atomic numbers. These atoms found in nuclear reactor moderators and include hydrogen (^1H) in light water, deuterium (^2H) in heavy water and carbon (^{12}C) in graphite [33, 39].

Inelastic scattering mainly occurs in fast neutrons when their energy is sufficiently high, causing nuclei (with large atomic number) to recoil which result in excitation due to the collision. The nuclei will de-excite thereby emitting γ -rays. In such a collision the neutrons lose a great amount of their energy. Fast or intermediate neutrons can be moderated (slowed down) to thermal/slow neutrons through such collisions. At room temperature, thermal neutrons reach thermal equilibrium with the absorbing medium [38, 39].

Neutron capture: Coulomb forces do not have any influence on neutrons (because of their charge neutrality); therefore, when slow neutrons approach nuclei they become captured by nuclei and completely disappear. Nuclear reactions occur as a result of this absorption. The type of nucleus and energy of the neutron is what determines whether the neutron can be captured [38].

2.3.4 Gamma radiation and effects on matter

Gamma (γ) radiation occurs when there is energy dissipation of the product nuclide (from a radionuclide decay process) from an excited (higher) energy state to a lower energy state. Nuclear isomers are referred to as nuclides in an excited energy state, and an isomeric transition is when these nuclides transition (decay) from a higher to a lower energy state. When in an excited state, gamma rays are emitted in discrete energies corresponding to the energy state transitions a nucleus may undergo [33, 38]. The amount of energy (E_γ) a gamma ray has is determined by the difference in energy states ($E_2 - E_1$) of the nuclear isomer which is given by Equation $E_\gamma = h\nu = E_2 - E_1$

(2-4) below.

$$E_\gamma = h\nu = E_2 - E_1 \quad (2-4)$$

where $h\nu$ (the product of Planck's constant and the frequency of the radiation) is the energy of the electromagnetic radiation [33].

Electromagnetic radiation like X-rays and γ -rays are known to be photons and they possess zero rest mass and charge. Photon interactions with matter differ from those of charged particles because of their charge neutrality. X-rays and γ -rays have longer ranges because they can travel for a while in matter before encountering an interaction; this is largely dependent on the photon energy and the medium which it is traveling in. Just like neutron, photons can be absorbed or scattered [35, 36].

Table 2-2: Difference between X-rays and γ -rays [33]

	X radiation	Gamma radiation
Energy	E < 1 MeV	E > 1 MeV
Production	Excitation and ionization	Nuclear reactions

Although there are many mechanisms in which photons interact with matter, there are three main ones which are as follows:

A. Photoelectric effect

The interaction that takes place during this process is one between a photon and an atomic electron. The photon gets absorbed and disappears; as a result, an electron is emitted from one of the atoms bound shells. The electron is known to be a photoelectron [34].

The wavelength of the photon rather than its intensity is what determines the energy of the emitted electron; shorter wavelengths mean greater electron energy. The greater the

photon energy, the most likely it is for it to emit the most tightly bound (K shell) photoelectron. The energy of the photoelectron is given by Equation $E_{e^-} = h\nu - E_b$

(2-5):

$$E_{e^-} = h\nu - E_b \quad (2-5)$$

where $h\nu$ is the photon energy and E_b is the binding energy. This means that the electron has been ionized, and to fill the vacancy an electron from an outer shell or a free electron will have to replace the ejected electron. This transition results in the release of energy, therefore characteristic X-ray photons may be produced [34, 38].

B. Compton Scattering

Compton scattering is an inelastic scattering process that takes place when a photon collides with an electron transferring part of its energy and causing the electron to recoil. The photon having an initial energy ($h\nu$), deflects at an angle Θ after colliding with an electron (assumed to be initially at rest), after then the photon will have an energy $h\nu'$. The electron having energy E_{e^-} , recoils at an angle ϑ [38, 39]. This is illustrated in Figure 2-5.

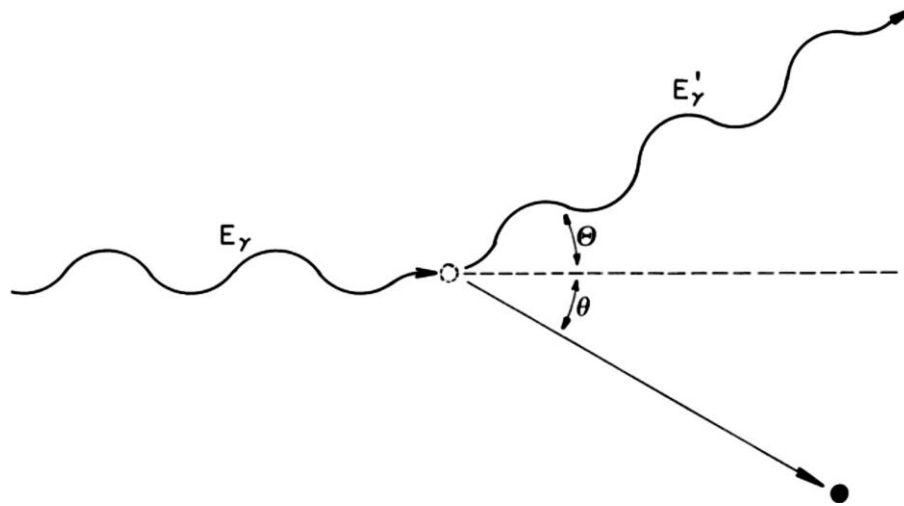


Figure 2-5: The Compton Effect. An incident photon collides with an atomic electron and imparts energy to it, the photon and electron being deflected at angles Θ and θ , respectively, to the trajectory of the incident photon [33]

C. Pair production

Pair production becomes possible when the energy of a γ -ray photon is more than twice the rest mass of an electron ($h\nu \geq 2mc^2$ or 1.022 MeV). The process takes place when a photon interacts with the Coulomb field of a nucleus, the γ -photon disappears thereby creating a production of an electron-positron pair. The nucleus itself does not experience any changes but its presence plays an important role in this mechanism [33, 39]. Figure 2-6 shows how a pair production is created.

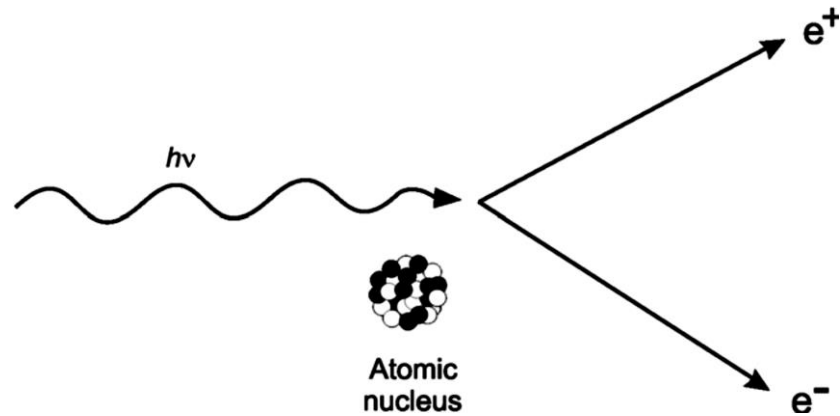


Figure 2-6: Pair production: The production of a negatron and positron pair by a gamma-ray photon [33]

Figure 2-7 shows a representation of the relationship between the three major electromagnetic interactions mentioned above. On the plot, three areas are described where the photoelectric effect, Compton scattering and pair production are dominant. The line between the photoelectric effect and Compton scattering is a representation of the energy at which the probability of both interactions as a function of absorber atomic number is equal. Consequently, the line between the Compton scattering and pair production represent equal probability of energy of both interaction mechanisms [33, 38, 39].

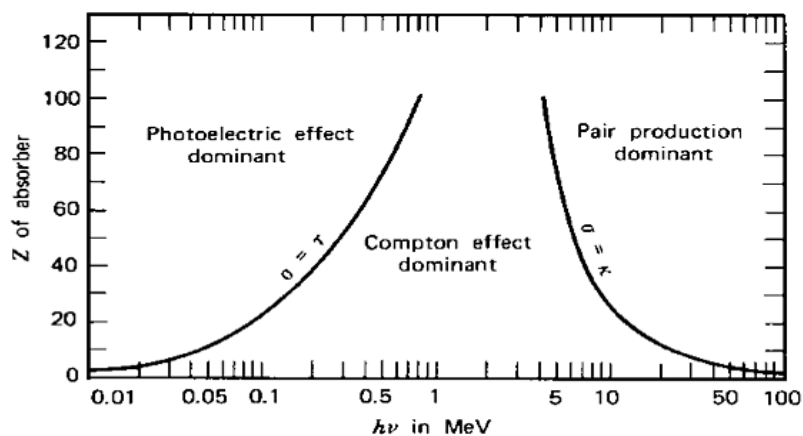


Figure 2-7: The relative importance of the three major x-ray and γ -ray interactions [40]

2.3.5 X-ray radiation and effects on PET

X-ray radiation is an electromagnetic radiation similar to gamma radiation. They are identical in their properties and they are both photons that possess a quantum of energy defined by reference [40]. The only difference between X-rays and γ -rays is their origin. X-rays originate from electron energy transition. The two types of x-rays are:

1. Characteristic x-rays are characterized by spectral lines of energy resulting from the transition of electrons in the shells (K, L, M....) of the atom from which they originate. When an electron from a given shell is displaced from an atom, an electron from an outer shell will fill the vacancy of the displaced electron that is when x-ray emissions are produced [33].
2. Bremsstrahlung x-rays are characterized as a broad smear of continuous energies, bremsstrahlung x-rays are produced by electrons or other charged particles (protons and alphas) when accelerated toward an atomic nucleus and are deflected by the Coulomb field of the nucleus [33].

2.4 Materials modification by ion implantation

The stopping of an energetic particle penetrating a solid is described by the energy loss rate dE/dx . The particle will undergo a series of collisions and subsequently loses its energy until it comes to rest within the target material [34]. The range, R , at which the ion will stop, is dependent upon the energy, mass, and atomic number and the density, mass and atomic number of the incident ion and the host material respectively [41]. The energy loss rate is determined by Coulombic interactions between the ion and the solid and is distinguished into two different mechanisms which are the

electronic (inelastic) and nuclear (elastic) collisions. These collisions are characterized by the energy regimes they dominate in [14, 41, 42]. These collisions lead to radiation damage which is a result of the destruction of the lattice atomic arrangement [42].

The depth at which the ion penetrates the solid is determined by dE/dx along the path of the incident ion. Many interactions occur when the incident ion traveling within the solid undergo collisions in its path, these interactions fluctuate statistically and are caused by the energy lost per collision. As a result; identical ions having the same incident energy will not come to rest at the same range. There is therefore a wide depth distribution where ions are embedded, this is referred to as the range distribution or range straggling [14, 41]. Due to their low scattering cross section, processes such as high radiation emission, secondary particles emission, charge exchange (between incident ions and target atoms) etc. that occur during ion implantation are negligible as they are not as significant as nuclear and electronic interactions [42].

2.4.1 Ion stopping powers in matter

The rate of energy loss is expressed by the Equation 2-6.

$$S = \frac{dE}{dx} = \left(\frac{dE}{dx}\right)_n + \left(\frac{dE}{dx}\right)_e = S_n + S_e \quad (2-7)$$

where S represents the total ion stopping power, E is the incident energy of the ion traveling in the solid, and x is the penetration depth which the ion will stop at. The subscripts n and e denote nuclear and electronic stopping power respectively. The final distribution of ions in a target material and the defects caused by these energetic ions are determined by the ion stopping power [14, 42]. Since there are two mechanisms at which the ions lose their energy, it is therefore important to understand the processes ions undergo before they come to rest in the substrate, which effects these processes (nuclear and electronic collisions) have on the final distribution of ions.

Nuclear collisions cause atoms in a lattice to be displaced thereby creating a disorder in the lattice. The trajectory of the incident ion changes significantly due to a large amount of energy loss. While in electronic collisions, the angular deflection is insignificant and the lattice disorder is negligible due to smaller energy losses [42]. Though acting simultaneously; these processes are independent of each other, hence the separation in the above equation.

Figure 2-8 describes the total stopping power as a function of ion velocity (proportional to the ion energy) over a wide energy range. Figure 2-8 is discussed in section 2.4.1.2.

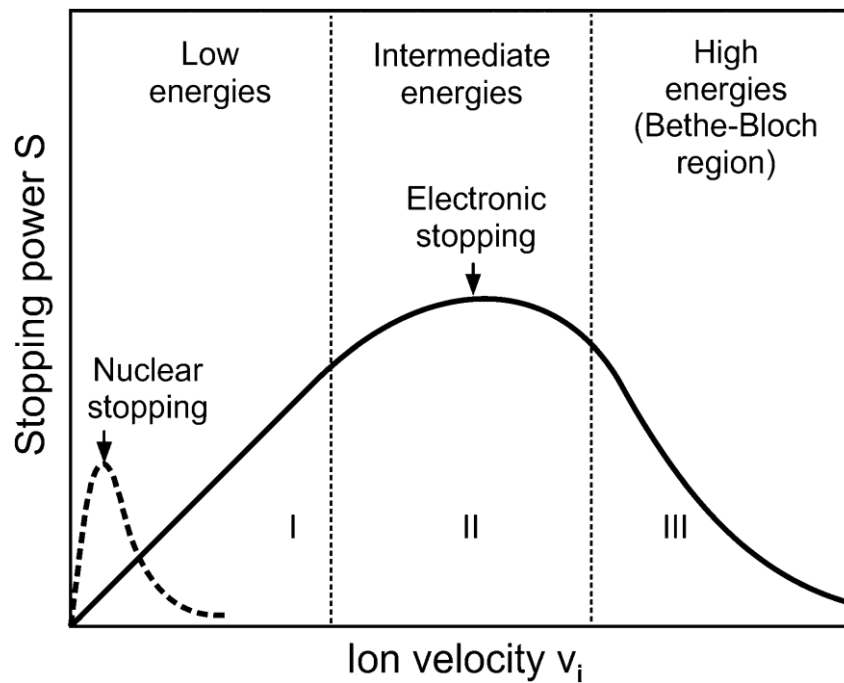


Figure 2-8: Nuclear and electronic components of the ion stopping power S as a function of ion velocity [43].

2.4.1.1 Nuclear stopping power

Energy loss in this process is a result of elastic collisions that occur between the incoming ions with the target atoms. The potential $V(r)$, between an ion and the target atom describes the nuclear scattering process. When there is repulsion between the ion and the target nuclei and the incoming ion backscatters; the interatomic potential of the two positive charges is given by:

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \quad (2-8)$$

where Z_1 and Z_2 are atomic numbers of the ion and the target respectively, e is the electron charge, ϵ_0 is the permittivity of free space and r is the interatomic distance. This potential does not consider the screening effect as it is a pure Coulomb interaction potential [14, 43]. The Coulomb potential can be corrected by a screening function, f_s :

$$V(r)_{corr} = V(r) \cdot f_s \quad (2-9)$$

From the above equation, the screening angle ϑ for any incident ion trajectory can be calculated. The energy transfer rate, E_T , of the nuclear collisions per unit path length can be calculated. For $E_{T, max}$, which is the maximum possible transfer energy, S_n can then be written as:

$$S_n = \left(\frac{dE}{dx} \right)_n = N \int_0^{E_{T, max}} E_T d\sigma \quad (2-10)$$

where N is the number of target atoms per unit volume and σ is the differential cross section.

Target atoms may be displaced from their atomic lattice by the energy transfer from the bombarding ions, this interaction creates damage and defects to the crystalline lattice [43].

2.4.1.2 Electronic stopping power

Inelastic collisions causing the electronic stopping of projectile ions result in excitation and ionization of the target electrons. The theoretical models of this mechanism are complex as they result from different processes (excitation of conduction electrons, direct kinetic energy transfer to electrons due to electron-electron collisions, excitation/ionization of the target, and excitation/ionization/electron-capture of the projectile ion itself) [14]. Electronic stopping can be described by breaking it down into three energy regions. The distinction is done by comparing the ions velocity with the Bohr velocity, $v_0 = e^2/\hbar$, where e is the electron charge and $\hbar$ is Planck's constant. The regions depicted in Figure 2-8 on page 26, are as follows:

- i. Low energy region – the slowing down of ions can be described as a “viscous drag” force which is proportional to the velocity of the ions. Not enough energy can be transferred by the ion to electrons having energies that are lower than the Fermi level; i.e. excitation cannot occur. Electrons with energies, $E \approx$ Fermi level can only contribute to the energy loss. Here, $v_1 < v_0 Z_1^{2/3}$, where v_1 is the velocity of the ion, v_0 is the Bohr velocity and Z_1 is the ion's atomic number. The projectile ion gradually loses its energy through a cloud of electrons into thermal vibrations of the target atoms.
- ii. Intermediate energy region – S_e reaches its maximum and the ion is partially ionized. In this region $v_1 \approx v_0 Z_1^{2/3}$.
- iii. High energy region – the Bethe-Bloch region where $v_1 > v_0 Z_1^{2/3}$. At such high ion velocities/energies the ion's charge state increases and thereby becomes fully stripped of its electrons. With further increasing projectile velocities, the S_e decreases due to short ion-target interaction [14, 41, 42, 43].

2.4.2 Ion range and range straggling

An ion's path to its final resting place in the target material involves interaction with several atoms/electrons of the target, ultimately causing collisions along the way and subsequently losing its energy. Each ion's path varies from the other as they have different collision sequences, subsequent ion deflection and total path length because the process of the ion stopping is random and therefore results in a zigzag path of the ion. As a result of these random processes, ions having the same incident energy and angle will not come to rest at the same place [41, 42, 43].

Since the ion experiences a series of collisions; it does not travel in a straight line until it comes to rest. The range, R , is the actual distance that the ions has travelled before coming to rest in the target, whereas the projected range, R_p , is the total penetration depth of the ion into the material. R_p is perpendicular to the surface of the target material. This is depicted in Figure 2-9.

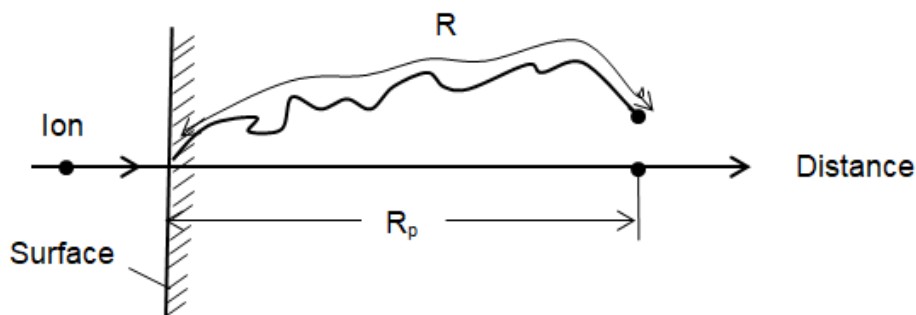


Figure 2-9: An ion incident on a semiconductor penetrates with a total path length R , which gives a projected range R_p along the direction parallel to that of the incident ion [41].

The distribution of many ions is therefore statistically broad in penetration depths. Range distribution or range straggling is known to be the distribution in projected ranges on the implants [42]. The concentration, $N(x)$ of the implanted ions as a function of depth x is directly proportional

to the dose (number of ions per unit area) ϕ , and can be approximated by a Gaussian distribution.

$N(x)$ is expressed as:

$$N(x) = \frac{\phi}{\Delta R_p (2\pi)^{\frac{1}{2}}} \cdot \exp \left[-\frac{1}{2} \left(\frac{x - R_p}{\Delta R_p} \right)^2 \right] \quad (2-11)$$

where R_p and ΔR_p are the projected range (mean distribution depth) and the projected range straggling (standard deviation of the distribution) respectively. The simplest approximation to describe the distribution of ion range is represented by the Gaussian approximation for $N(x)$. Although less accurate for higher energies, the approximation to the profile for lower energies is good. Profiles at higher energies become asymmetric [41, 43].

2.4.3 Ion induced radiation damage

The displacement energy, E_d , is the minimum energy (threshold) required to displace an atom from its lattice site by an energetic ion traveling in the crystalline target. The disorder/disruption in arrangement of the lattice as a result of ion implantation is called radiation damage [42].

As energetic ions travel through a target, a series of electronic collisions takes place (high energy regime) and as they decelerate; the ions transfer their kinetic energy and momentum to the target atoms resulting in nuclear collisions at a lower energy regime where these collisions (elastic/nuclear) become dominant. Damage or disorder to the target atoms is only due to nuclear collisions; during these collisions the ions may transfer enough energy to cause displacements of target atoms (energetic recoil lattice atoms) [33]. The displaced atoms are referred to as primary knock-on atoms (PKAs). These atoms can in turn displace other target atoms known as secondary knock-on atoms (SKA) from their lattice and SKAs will displace tertiary knock-on atoms and so on, thereby creating displacement/collision cascades. Along the ion track, these displacement

cascades create an agglomeration of vacancies and interstitial atoms and other types of lattice defects. A Frenkel pair is known to be a vacancy-interstitial defect and it is defined as the removal of an atom (creating a vacancy) from its lattice position and occupying an interstitial position. Frenkel (vacancy-interstitial) pairs are created when the damage energy, T_d (energy transfer during an elastic collision), exceeds the displacement energy, E_d [33, 38, 41, 42]. This radiation damage theory is illustrated in Figure 2-10.

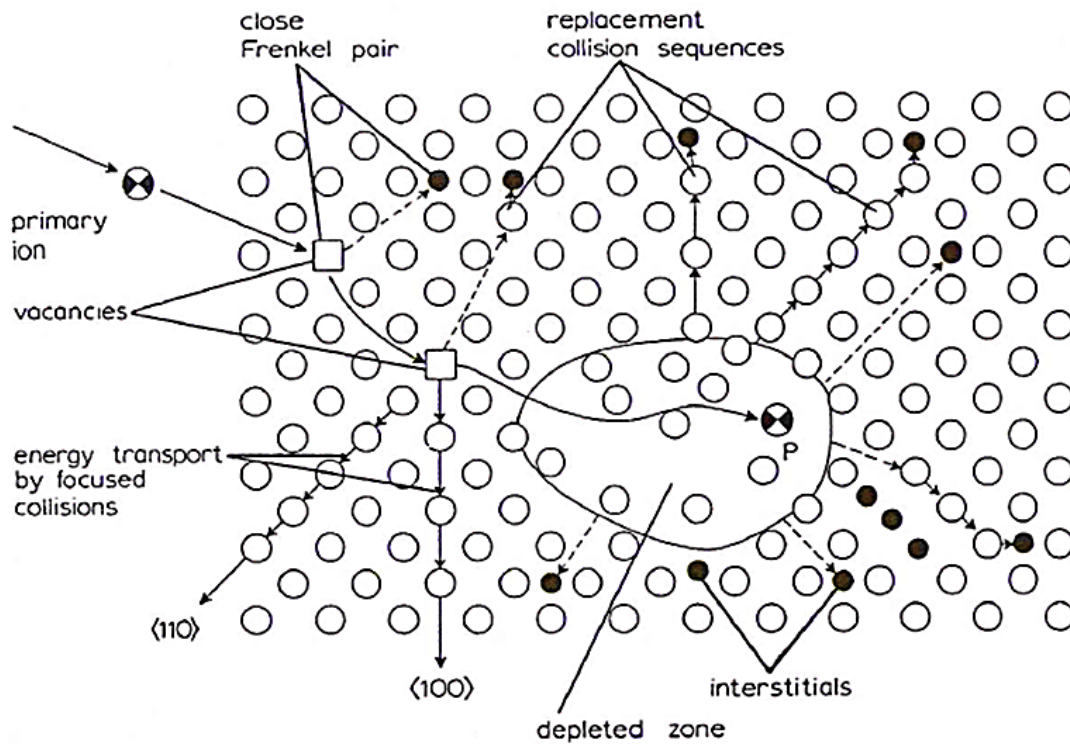


Figure 2-10: A schematic representation of the collision cascade process showing the collision cascade and the focused collision sequence extending beyond the main cascade regime [42].

With an increase in the number of ions incident on the target (increase in ion fluence); the disordered volumes begin to overlap thereby leading to the formation of a heavily damaged (amorphous) layer. The amount of damage on the target and the depth distribution, $N_d(x)$, is

dependent upon the ion-target mass ratio M_i/M_t , ion specie, ion energy, temperature, fluence and the current density [42, 43].

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 Introduction

Chapter 3 outlines the preparation of PET samples, the experimental procedures and techniques which were used for the characterization of implanted PET samples. Characterization techniques such as FTIR, Raman and XRD provide information about the material structure. Information about the enhancement of the conductivity of the PET foils was obtained from UV-Vis and I-V measurements. Additional information on the morphology and depth profiles of the implanted ions was obtained from SEM (EDX) and ERDA measurements, respectively.

3.2 Sample preparation

A sheet of commercial PET (Mylar) supplied by Sigma-Aldrich was cut into sizes of $8 \times 8 \text{ mm}^2$, $10 \times 10 \text{ mm}^2$ and $15 \times 15 \text{ mm}^2$. The samples were washed and prepared for ion implantation at the Accelerator Mass Spectrometry (AMS) lab situated at iThemba LABS (TAMS). At two minutes intervals, the samples were submerged in small amounts of acetone, ethanol and distilled water, in that order, and thereafter dried using nitrogen gas. This process was done so as to clean the samples and eliminate any debris that might contribute to the results.

3.3 Ion implantation

3.3.1 Basics on ion implantation

The basic function of an ion implanter is to accelerate a beam of ions of a particular atomic species at a certain voltage and to direct this beam so that the ions can be evenly implanted across the surface of a target material. Figure 3-1 shows a schematic representation of an ion implanter. The following paragraphs give a brief description of the operating principles of an ion implanter; this information is given in ref [44].

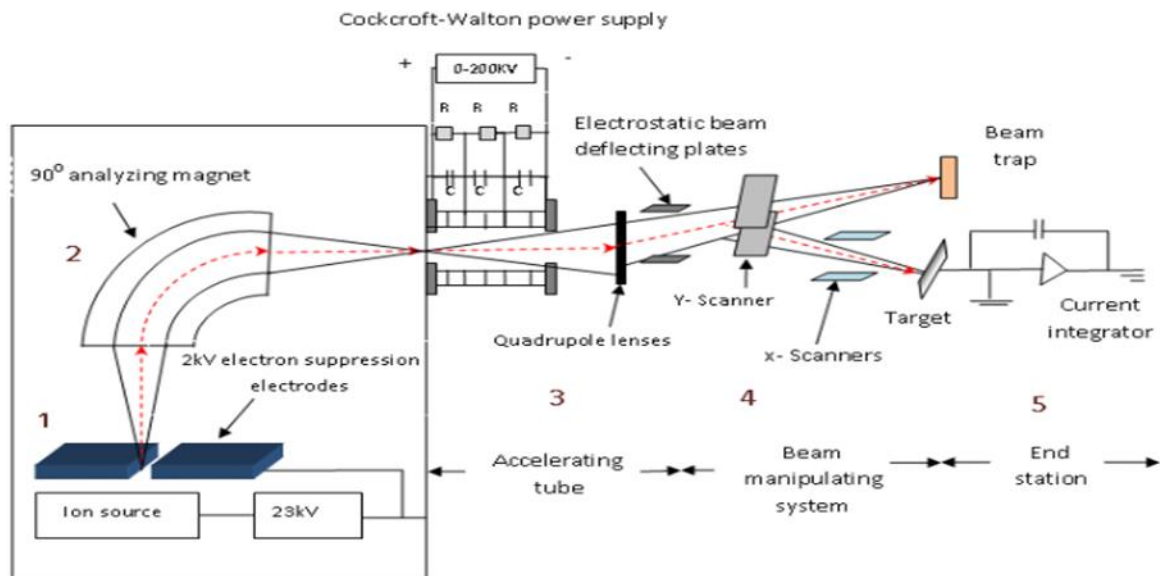


Figure 3-1: Schematic diagram of the Varian Model 200-20A2F ion implanter [44].

An arc discharge ion source is used to produce ions; this arc discharge is maintained by a source of carrier gas leaked into the chamber. Gas molecules break into different species of positively charged ions when the carrier gas molecules collide with electrons from the hot cathode arc discharge. The extraction of ions from the chamber is by means of an electrical potential between

the source exit aperture and the extraction electrode (placed outside the chamber). A potential difference between the source and the electrode causes the extraction of ions through a slit. As the ions are accelerated through the voltage difference they gain energy. The energy of a particular ion is given by:

$$E = QV$$

where Q is the charge of the ion and V is the potential difference between the electrode and the source. Consequently, ions with a double charge will produce twice the extraction energy [44].

Different ion species make up the beam, and because of this, the desired ion specie needs to be separated and selected for the implantation process to take place. The analysing magnet is designed for the separation process by varying the magnetic field strength. The ion beam enters a region of transverse magnetic field where ions get deflected into circular orbits after leaving the source. The atomic mass of the ions is what determines the amount of deflection. The magnetic field is tuned such that the desired ions are deflected through a 90° angle and focused at a resolving aperture by the magnet. Other ions in the beam will be deflected through angles greater or less than 90° and will be collected at the magnet chamber walls. The intensity of the beam is adjusted by means of a variable slit located just after the resolving aperture [44].

The high voltage terminal is maintained at high potential during operation. The resolving aperture and variable slit are contained here. The terminal is housed in a grounded enclosure with safety interlocks because of the high potential. The ion beam enters an accelerating tube (with a variable high potential of up to 180 kV) after leaving the analysing magnet, and here ions in the beam are accelerated to a greater energy before being implanted. Ions are attracted towards the exit, accelerating to their final energy. A quadrupole doublet lens is positioned just after the accelerating tube as the ion beam diverges; the beam is then focused into an oval shape spot [44].

Two sets of electrostatic deflection plates scan the beam to ensure even distribution of ions on the target material. In order to scan the ion beam vertically at 117 Hz and horizontally at 1019 Hz, the deflection plates require high voltage [44].

The ion beam finally reaches the implant chamber where the implantation takes place. Ions striking the material produce a residual electric current which is used to determine the ion dose on the material. The beam is removed from the implant chamber when the selected dose has been measured [44].

3.3.2 SRIM simulation

The physical principles behind ion implantation are discussed in Section 2.4 and therefore SRIM is a tool that was used to further understand these principles. For practical purposes semi-empirical codes like SRIM2013 [45] have been developed over the years to estimate ion penetration depths and damage distribution in the target material. SRIM2013 simulation was used in this work to predict the range at which the projectiles, Ti^+ and Ar^+ ions, will implant within a PET matrix, and in turn help with the selection of the energy at which these ions should be accelerated to the target material. Figure 3-2 and Figure 3-3 show the ion range and collision/damage events of 100 keV Ar^+ and Ti^+ ions, respectively.

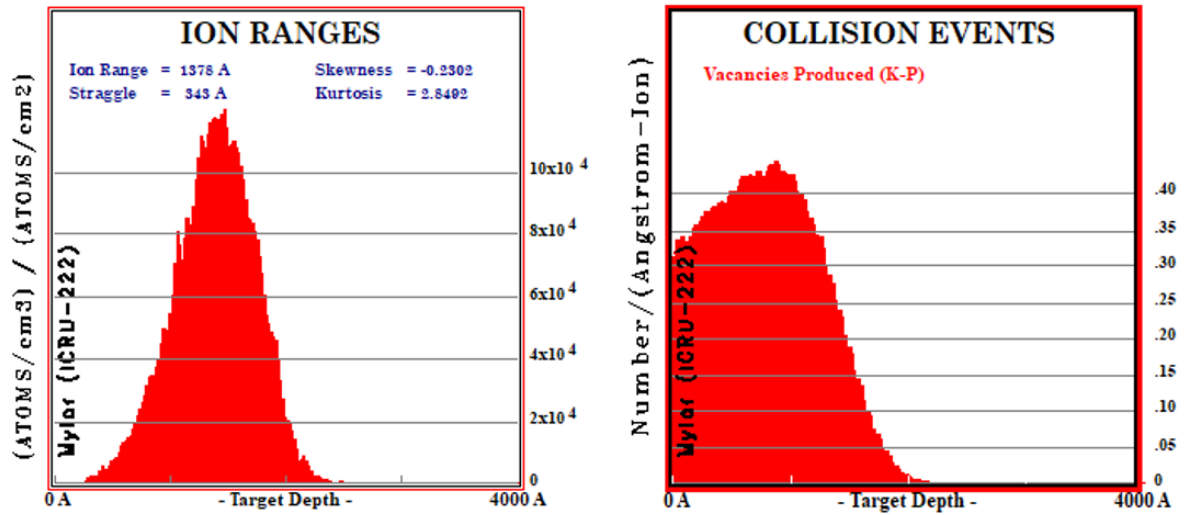


Figure 3-2: Ion range and damage events of 100 keV incident ions (Ar^+) in PET target (TRIM simulation for 10,000 ions).

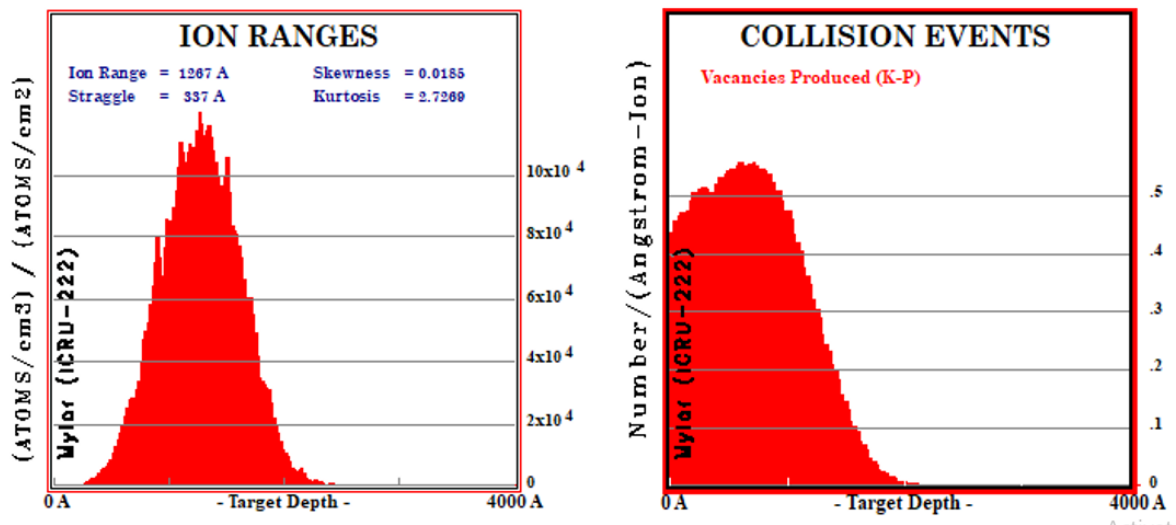


Figure 3-3: Ion range and damage events of 100 keV incident ions (Ti^+) in PET target (TRIM simulation for 10,000 ions)

SRIM2013 shows that the range for 100 keV Ar^+ ions in PET is 1373Å (0.1373μm) and for 100 keV Ti^+ ions the range is predicted to be 1267Å (0.1267μm). Since the thickness of the

film is 130 μ m, compared to the ranges predicted by the program, it is apparent that only the sub-surface region of the PET film will be modified. Implantation to depths well below the surface (> 100 nm) also ensured that any changes observed would have been due to the interaction of the implanted species with the PET matrix and not the surface reacting with the ambient environment.

3.3.3 PET film implantation

Transparent PET thin films (density = 1.397 g/cm³) were fixed onto a sample holder which was cooled to cryogenic temperatures. The films were implanted at liquid nitrogen temperature (-196 °C to -210 °C) using the Varian 200 – 20A2F ion implanter located at iThemba LABS (Gauteng). Ti⁺ and Ar⁺ ions were each implanted at an energy of 100 keV to fluences of 2×10^{16} , 8×10^{16} , 1×10^{17} , 1.4×10^{17} and 2×10^{17} ions/cm². An implantation current of 4 μ A was kept constant for all the implantation fluences. With a current as high as 4 μ A, the material was cryogenically implanted so as to determine whether temperature has an effect on the degree of beam induced damage within the PET matrix.

3.4 Characterization techniques

3.4.1 X-ray diffraction spectroscopy (XRD)

One of the methods that can be used to study the structure of solids is X-ray diffraction. In this method, X-rays of a specific frequency are used to interact with materials so as to determine the diffraction pattern and for the acquisition of values of lattice parameters [46]. It is then important to understand Bragg's equation when analysing diffraction data.

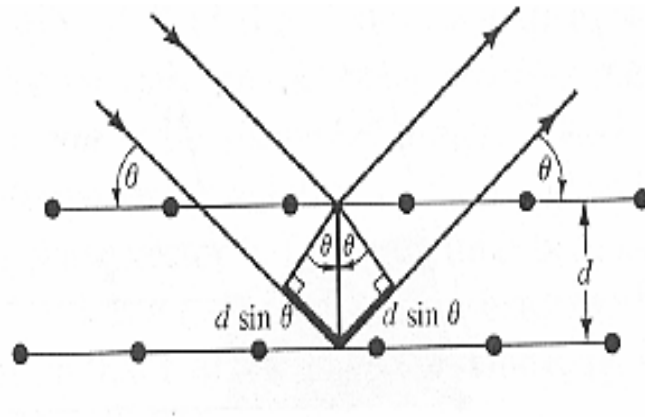


Figure 3-4: Illustration of the Bragg diffraction [47].

Consider a crystal that is made out of parallel planes of atoms/molecules/ions, and are spaced a distance d apart. A sharp peak of the intensity of the scattered radiation will have the following conditions:

1. X-rays should be reflected by the atoms/molecules/ions in one of the planes
2. Constructive interference should occur from the X-rays that are reflected from successive planes

The path difference between the two X-rays that are reflected from the two consecutive planes is given by:

$$2d\sin\theta$$

The path difference must be an integral number of the wavelength λ in order for the X-rays to interfere constructively, Bragg's equation is therefore given by:

$$n\lambda = 2d\sin\theta$$

where n is a positive integer, λ is the wavelength of the X-ray, d is the interplanar spacing and θ is the incident glancing angle. The diffraction can only occur if the above equation is satisfied [47].

3.4.1.1 Working principle of XRD

A basic XRD instrument consists of three main components, which are X-ray source, sample holder and detectors; Figure 3-5 shows a set-up of the XRD instrument [48].

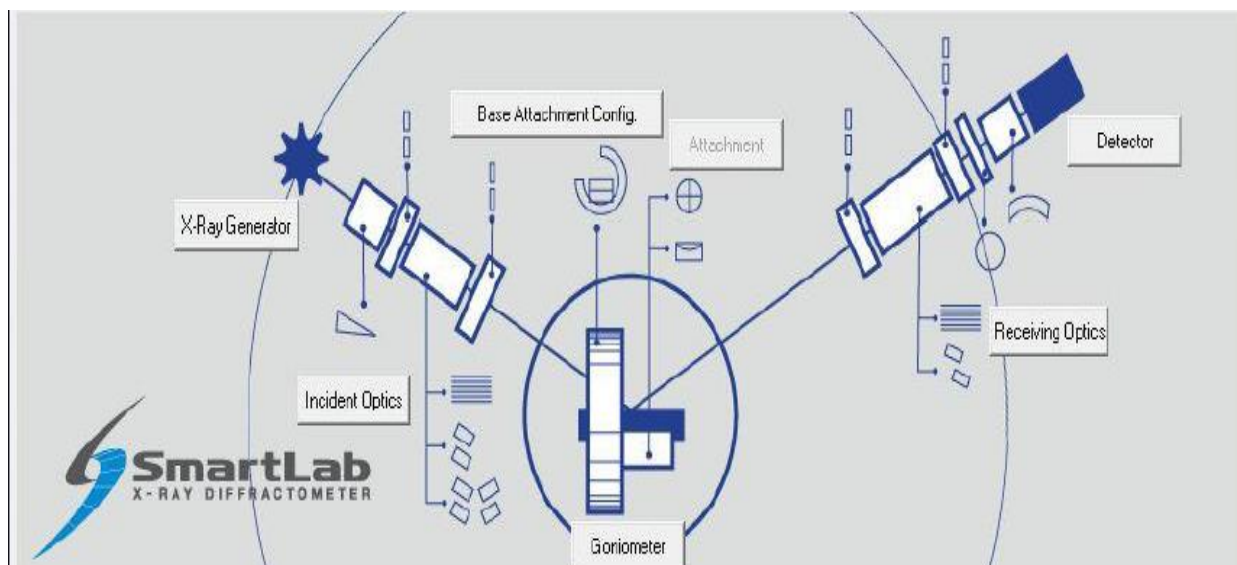


Figure 3-5: Schematic diagram of XRD set up [48].

In a cathode ray tube, X-rays are generated by heating a filament to produce electrons; the target material is bombarded with electrons which are accelerated to the target by applying a voltage. Inner shell electrons are knocked off the target material when electrons from the target source have sufficient energy; characteristic x-rays are then produced. Most common components these spectra consist of are K_{α} and K_{β} . Wavelengths are characteristic of the target material, in many instances the target material can be either of Cu, Fe, Mo or Cr [48]. Monochromatic X-rays are needed for diffraction, these can be produced by using foils and crystal monochrometers for filtering, X-rays are then collimated and directed to the sample. The geometry of an X-ray diffractometer is such that the sample rotates in a path of the collimated X-ray beam at an angle of Θ while the X-ray

detector is mounted on an arm to collect the diffracted X-ray and rotates at an angle of 2θ (data is collected at 2θ from 5° to 70°). The intensity of the reflected X-ray is recorded as the sample and detector are being rotated (goniometer is the instrument used to maintain the angle while rotating the sample). A peak intensity and constructive interferences occur when the geometry of the incident X-ray colliding with the samples fulfil the Bragg Equation. The X-ray signal is converted to a count rate by the detector, and the output is given on a printer or computer monitor [48].

In this study the Rigaku SmartLab X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used to investigate the crystallinity of pristine and implanted PET thin film samples. In the measurement, an X-ray beam is directed to a sample, and the X-rays are diffracted through the crystal and into a detector. The beam and the detector are rotated through a range of angles. The angles at which the beam is diffracted by the crystals correspond to the planes of the crystal. Each crystal has a corresponding intensity of the diffracted beam and has a characteristic pattern of diffracted angles [48]. The measurements were performed using grazing incidence geometry.

3.4.2 Scanning electron microscope (SEM)

3.4.2.1 Principle of SEM operation

A schematic representation of a SEM is shown in Figure 3-6.

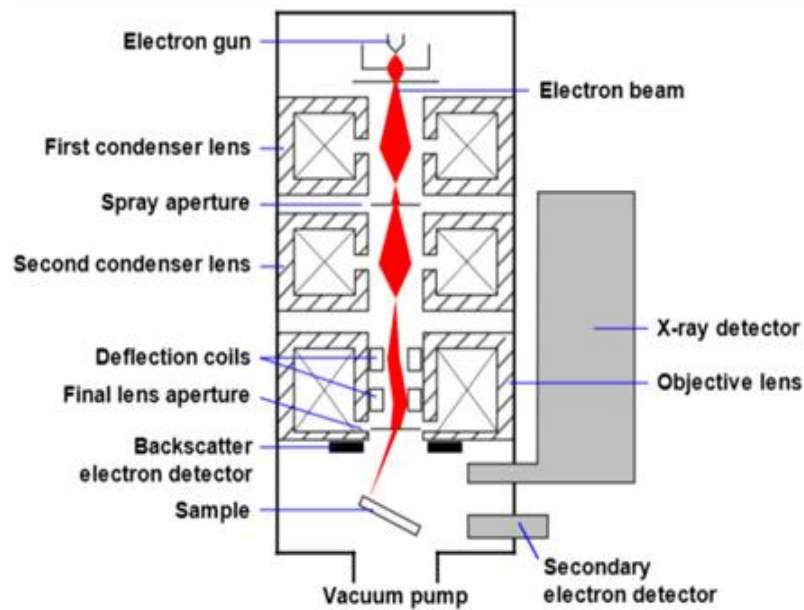


Figure 3-6: Schematic representation of a basic scanning electron microscope [49].

The SEM instrument is made up of many different components that play different roles towards generating an image that gives information about the composition and topography of the sample under investigation. The following are the main components of a SEM:

- Electron source (gun)
- Lenses
- Scanning coil
- Sample chamber
- Detectors
- Display unit

An electron beam is produced when a high electric field is applied to a metal plate (extracting electrode) caused by the field emission effect. A field emission gun (FE gun) is a tungsten wire (called the emitter) with a radius of 100 nm (or less); a schematic set up of a field emission gun

(Figure 3-7) is shown below. A tunnelling effect occurs when a positive voltage of a few kV is applied to the extracting electrode thus electrons are produced from the emitter. A FE electron gun is suitable for high-resolution SEM because the electron beam emitted from the emitter behaves as though it was produced from an electron source of 5 – 10 nm in diameter. The energy spread of the electron beam is small and therefore the FE gun does not require heating. FE guns operate under ultrahigh vacuum of about 10^{-8} Pa [49, 50].

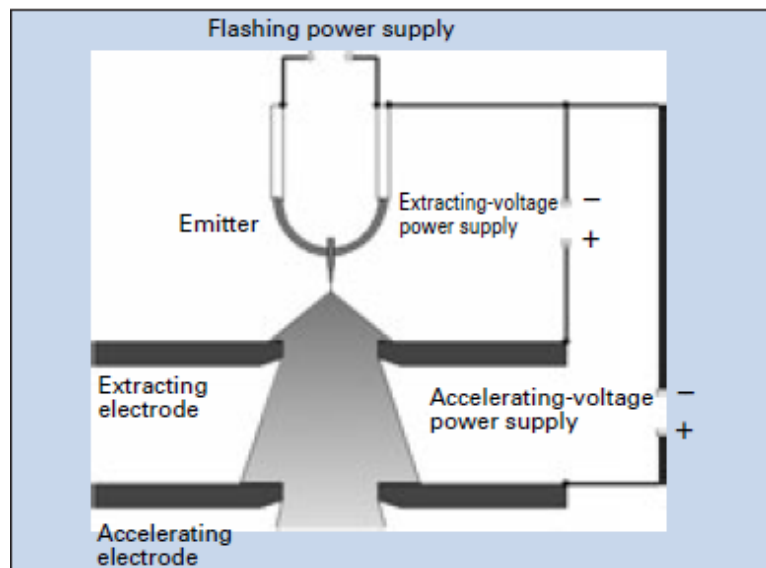


Figure 3-7: Schematic representation of a FE gun [50].

The electron beam coming from the electron gun is focused by a series of lenses down the column as shown in Figure 3-7. These lenses allow electron beam diameter adjustments. The condenser and objective lenses are located below the electron gun, this two-stage lens focuses the electron beam and a small electron probe is produced. After the beam is focused, it is then deflected in the X and Y axes using scanning coils. This is done in a raster pattern over the surface of the sample. Samples are mounted and put in an evacuated chamber. The sample chamber may include a

translation phase, tilt and rotation devices, feed-throughs, optical cameras and a range of other devices to assist with sample processing. When the electron beam in a scanning electron microscope (SEM) interacts with a sample, multiple events occur. In essence, different detectors are required to differentiate between secondary electrons, backscattered electrons, or characteristic X-rays. The signals come from different penetration depths, depending on the accelerating voltage and sample density [49, 50].

To generate an image, a SEM scans the focused electron beam across the surface of a material. The interaction between the electron beam and the sample produces secondary electrons, backscattering electrons etc. and thus creates different signals that can be used to acquire information of the surface topography and composition. An image can be acquired from the detection of secondary electrons and the topography of the surface can be observed by a two-dimensional scanning of the electron probe over the surface [49, 50].

In SEM, an X-ray is emitted when the electron beam knocks off an inner shell electron that is replaced by an outer shell electron. This is known as characteristic X-rays because they are characteristic of individual elements and are therefore used for elemental analysis. Since each element has a unique energy difference between outer and inner electron shells, the X-rays that are detected can be used for elemental identification. X-ray Energy Dispersion Spectrometer (EDS) is used in SEM for element identification and composition [49, 50].

3.4.2.2 SEM measurements

In this work a JEOL 7800F (Field Emission Scanning Electron Microscope) with X-ray Energy Dispersive spectrometer (EDS) was used to determine the surface morphology and elemental composition of pristine and irradiated PET samples. Due to their insulating nature; PET films

(dimension = 8 x 8 mm²) were mounted onto a device where they were spun so as to coat them with carbon (graphite) to avoid charging. The coating was done using a sputtering process. The content of carbon in pure PET is 62.5%, EDX results show that carbon content has increased due to this process (see section 4.3.1). The SEM had the following measurement conditions/settings:

- Scanning voltage: 10 kV
- Scanning speed: 9 s
- Vacuum pressure: 0 torr
- Magnification: x 1600 – x 4300
- EDS take off angle: 30°

Scanning voltages of up to 20 kV measure the surface/subsurface of materials [51, 52]. SEM results are discussed in section 4.3.

3.4.3 Heavy-ion elastic recoil detection analysis (HI-ERDA)

Depth profiling Ti⁺ and Ar⁺ implanted PET thin films was done using a characterization method that is based on the detection of lightweight atoms that are recoiled from a target sample surface by a heavier high-energy ion beam that enters the surface at a grazing angle. This ion beam analysis technique is known as Elastic Recoil Detection Analysis (ERDA). Figure 3-8 shows the scattering geometry of a basic ERDA technique.

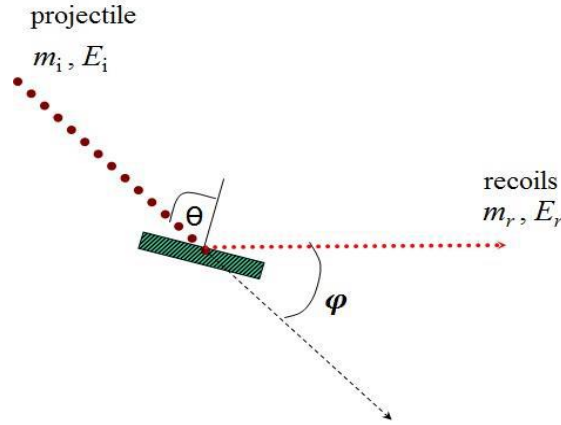


Figure 3-8: Schematic representation of the elastic recoil process showing the geometry of a scattering experiment [53].

Ion beam analysis at iThemba LABS (TAMS) is centred on a 6 MV tandem accelerator. The ion source used for heavy ion production is an 860 C sputter source with caesium gas as the source of sputtering ions. Heavy Ion (HI) ERDA comprises of detecting recoil atoms knocked off by a monoenergetic particle beam entering the surface at a grazing angle of incidence from the first few 100 nm of the target sample surface. Depending on the energy of the incident beam, the thickness of a target sample determines whether the monoenergetic particle beam can penetrate throughout the sample. The ejected recoils from the target sample are detected at a given scattering angle ϕ with respect to the incident beam, usually with a stopping foil in front of the energy detector [54].

The development of HI-ERDA was for the identification of atomic species and quantitative analysis of present elements in a target material, through generation of depth profiles from measured energy spectra [55]. Mass dispersive detector systems like the Time-of-Flight (ToF) spectrometer allow for separation of recoil ions according to mass and hence separate energy spectra. For depth analysis, elemental depth profiles are obtained from energy spectra through

both direct calculation codes like KONZERN and Potku [56], iterative simulation of elemental ToF spectra using Monte Carlo based codes like CORTEO [54].

Figure 3-9 shows the experimental set up of the ToF-ERDA system at iThemba LABS consisting of two timing detectors and an energy detector [53].

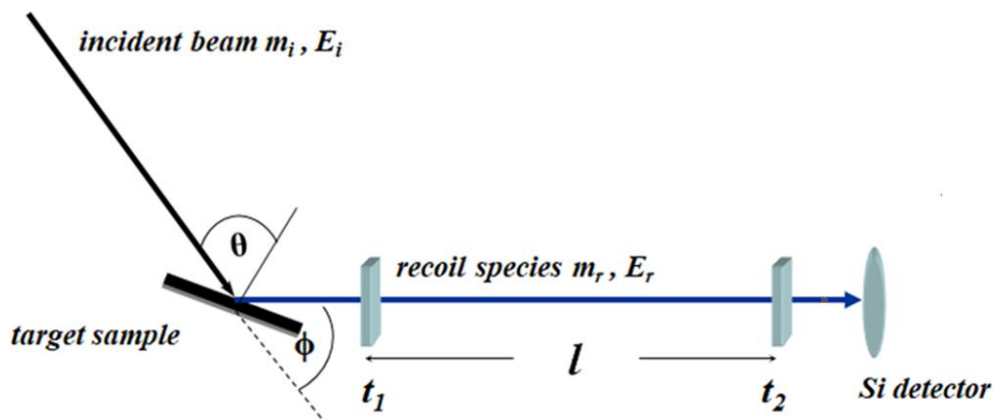


Figure 3-9: Schematic representation of the elastic recoil process showing the geometry of a scattering experiment. The incident particles bombards a specimen at an angle Θ to the sample surface normal, and the recoils are scattered an angle Φ and travel through two timing detectors (t_1 and t_2) and stop in the (Si) energy detector [53].

The ToF spectrometer sits at 30° to the incident beam direction and consists of two micro-channel plate (MCP) timing detectors based on $9.0 \mu\text{g}/\text{cm}^2$ thick carbon foils which are separated by a distance $l = 0.6 \text{ m}$. There is a passivated implanted planar silicon (PIPS) energy detector at the end of the flight path just behind the second time detector. Secondary electrons are ejected from the carbon foil when ions pass through the foil; these electrons are then directed to the MCP by an

electric field. A timing output signal is given off by the multiplication of electrons caused by the MCP. The timing output signal is then directed to a constant fraction discriminator. The signals from the timing detectors are then fed into a time-to-digital converter. The electronics for signal processing consists of conventional Nuclear Instruments Modules that include constant fraction discriminators for fast timing, time-to-digital converter, and analog-to-digital converter for the PIPS detector signal. The data acquisition system is based on the freely accessible MIDAS data acquisition platform, which has been internally customized for this set-up. Coincidence measurement of the ToF and recoiled ion energy, with the PIPS detector providing the trigger signal facilitates separation of detected atomic species according to their mass [53, 54, 55].

In a ToF-ERDA experiment, a particle's time of flight with mass m_r and energy E_r is given by [53]:

$$ToF = l \left(\frac{m_r}{2E_r} \right)^{1/2} \quad 3-1$$

where l is the length between the two carbon foils. Every recoil ion passing through the first carbon foil will experience some energy loss, therefore the correct ToF can then be rewritten as [53]:

$$ToF = l \left(\frac{m_r}{2(E_r - S(E_r) * x)} \right)^{1/2} \quad 3-2$$

where x and $S(E_r)$ are the thickness of the carbon foil and energy loss rate (or stopping force) of the particle traveling through the first carbon foil.

The ToF-ERDA measurements may be obtained from a bi-parametric display of ToF vs Energy.

The ToF spectra of the detected recoils are converted to energy using the equation [53]:

$$E_r = \frac{1}{2} m_r \left(\frac{1}{\text{ToF}} \right)^2 \quad 3-3$$

from which depth profiles are then calculated. The codes (KONZARD and Potku) used make use of SRIM [45] stopping force data and Rutherford recoil cross sections to convert energy spectra into depth profiles. Examples of profiles (ranging from 70 – 200 nm) obtained in this work, from the analysis of ion implanted PET using 18 MeV Cu⁵⁺ incident ions are shown figures Figure 4-9 to Figure 4-13 in section 4.4.

3.4.4 Fourier transform infrared spectroscopy (FTIR)

3.4.4.1 Background of infrared spectroscopy

Infrared (IR) spectroscopy is a powerful technique which provides fingerprint information on the chemical composition of samples, it involves the study of interactions between matter and electromagnetic (EM) fields in the IR region [57]. In the IR region, the EM waves pair with molecular vibrations; when the IR radiation is absorbed by the molecules, the molecules get excited to higher vibrational states [58, 59]. The absorption frequency depends on the vibrational frequency of the molecules, whereas the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule, and this depends on the change in the dipole moment that occurs as a result of molecular vibration [57]. The interaction between the frequency and the molecule determines the probability of a specific IR frequency being absorbed, meaning; if the photon energy of a particular frequency coincides with the vibrational energy levels of the molecule, the frequency will be greatly absorbed [59]. Fourier Transform Infrared (FTIR) spectroscopy can be used for quantification of several components absorbing in the mid infrared region (400-4000 cm⁻¹).

FTIR provides information on how well ion implanted PET absorbs and emits IR radiation. This technique indicates bond breakage, chain scissions, cross-linking and etc. by functional groups thereby indicating carbon cluster network formation. Chapter 4.5 provide the results and discussions on FTIR measurements.

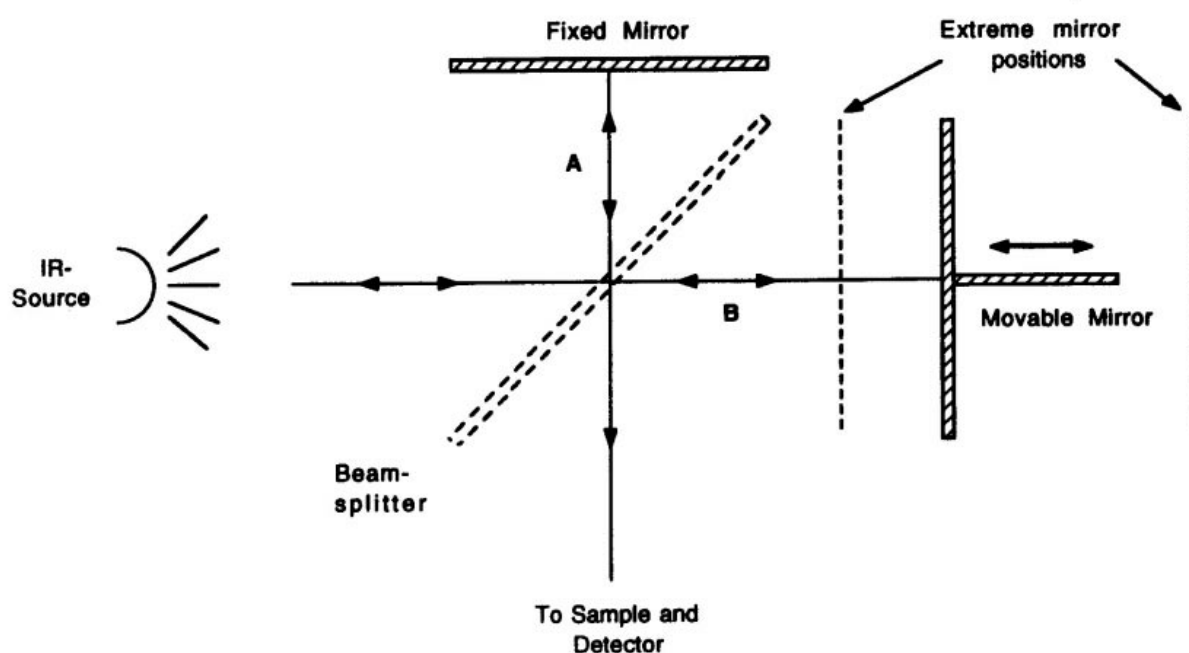


Figure 3-10: A schematic representation of a Michelson interferometer [57].

Working principle of an interferometer

Infrared radiation is directed to a beamsplitter (an ideal beamsplitter consists of a non-absorbing film), where half of the radiation is transmitted to a moving mirror which moves back and forth at a constant speed, and the other half of the radiation is reflected to a fixed mirror [57], shown in Figure 3-10. The two beams then recombine at the beamsplitter after being reflected from the mirrors. The beams are then directed to the detector, these two beams reaching the detector come from the same source. The position of the two mirrors determines the optical path difference of

the two beams (phase differences are fixed). Therefore, there are interferences between the two beams. By positioning the moving mirror, the two beams can be made to interfere constructively or destructively for a particular frequency. A cosine wave signal will be detected for a certain frequency when the moving mirror is scanned over that range, with the maximum and minimum corresponding to constructive and destructive interferences respectively. The cosine wave signal is called the interferogram – detector signal (intensity) against optical path difference. The source emits various frequencies therefore the output of the detector is the sum of all the interferograms [58, 59], shown in Figure 3-11.

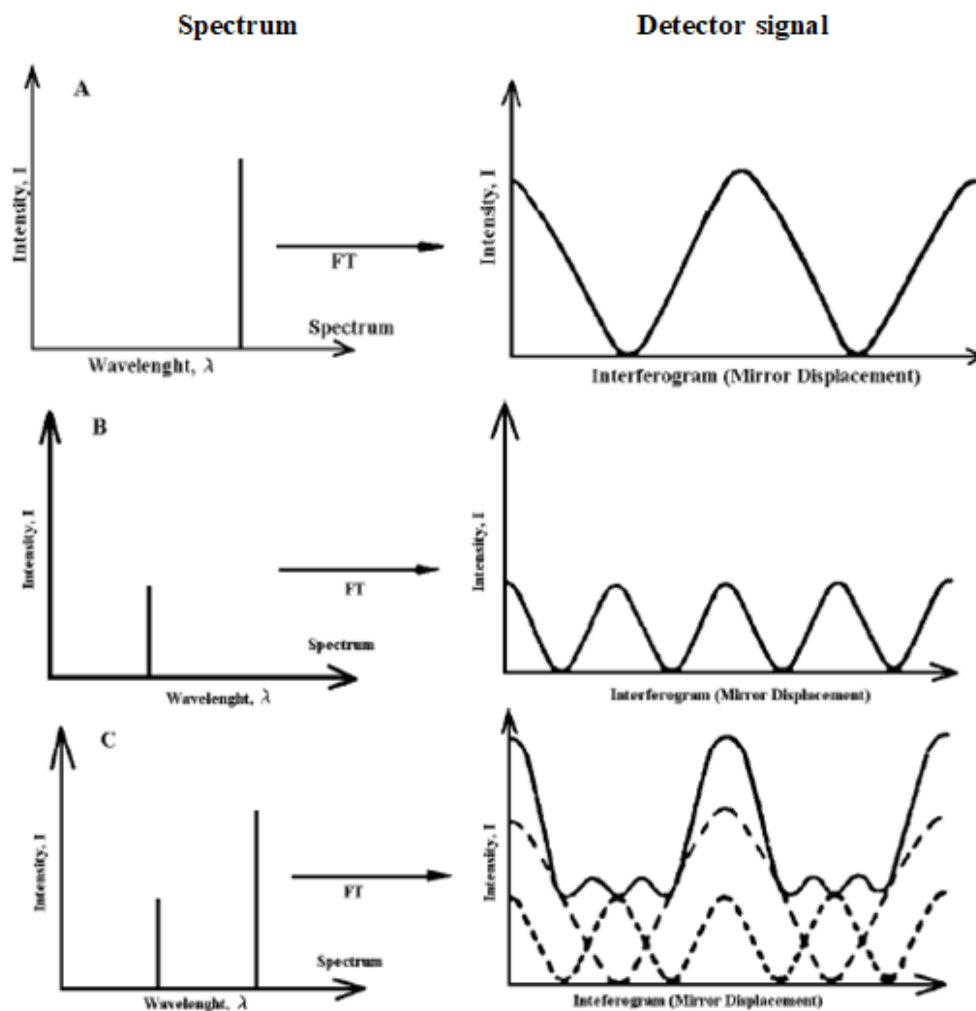


Figure 3-11: Relationship between spectrum and interferogram (detector signal) [57].

If the distance between the beamsplitter and the fixed mirror is y and the distance between the beamsplitter and the moving mirror is x , then the optical path difference (retardation δ) between the two beams is $2(y-x)$.

- A. If $y=x$, the retardation is zero and the beams are perfectly in phase, therefore all the light from the source will reach the detector as the two beam interfere constructively at the beamsplitter.
- B. If we consider a different line source where the frequency is doubled or the wavelength is half of the original line source. Here the amplitude of the cosine wave is equal to the intensity of the line source, while the frequency or wavelength of the line source relates to the frequency of the cosine.
- C. When placing the two line sources through the interferogram simultaneously, each line source will generate its own interferogram. The line sources will be measured together in the instrument and the end result will be the sum of the two individual line sources [57].

In FTIR spectroscopy, interferogram is determined experimentally. The transmittance (%T) values are plotted against the corresponding wave number (cm^{-1}) to produce a spectrum. The spectrum is displayed as this transformation is carried out automatically. Infrared spectroscopy results in a positive identification (qualitative analysis) and in the spectrum the peak sizes are a direct indication of the number of material present [58].

3.4.4.2 FTIR measurements

In a FTIR instrument, there is an interferometer, usually of Michelson type. In the interferometer, a beam of radiation is divided into two beams by means of a beamsplitter. The beams are

recombined after traveling two different paths. In this way, interference between the beams is obtained and the intensity of the output beam from the interferometer can be monitored as a function of path difference using an appropriate detector [57]. In this work, the IRTracer-100 FTIR spectrophotometer was used to investigate the chemical structure of both implanted and pristine PET samples and typical spectra obtained for PET are shown in figures Figure 4-15 to Figure 4-18 on pages 76 to 82.

3.4.5 Ultraviolet-Visible spectroscopy (UV-Vis)

UV-Vis spectroscopy is a technique based on the absorption of light by a sample, where electromagnetic waves (UV, Visible and near IR) are used to interact with the sample. The light can be partially absorbed depending on the sample, the remaining light is transmitted and is recorded as a function of wavelength by a detector, where the samples UV-Vis spectrum is produced. The absorption spectra are achieved by means of a spectrophotometer [60]. A schematic representation of a UV-Vis spectrophotometer is shown in Figure 3-14 on page 56.

The PerkinElmer Lambda 365 UV-Vis spectrophotometer was used to investigate how PET samples absorb light in the ultraviolet (UV) and visible region as well as to determine the energy band gaps of pristine and irradiated samples.

3.4.5.1 The absorption of ultraviolet rays and visible light

The absorption of ultraviolet and visible radiation is associated with the excitation of electrons in the atoms and molecules from lower to higher energy levels. Transitions from one energy level to another will cause light with the precise amount of energy to be absorbed because energy levels of matter are quantized [60].

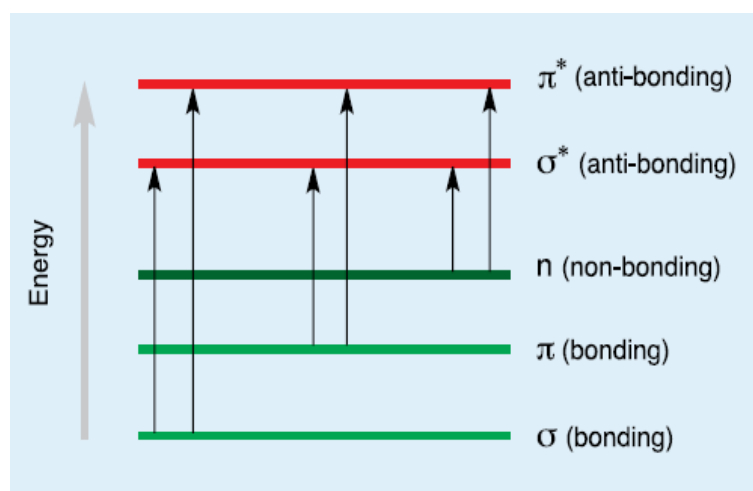


Figure 3-12: Electronic transition that light might cause [60].

In all cases, an electron is excited from a low energy level (full orbital/ground state) to a higher energy level (empty anti-bonding orbital/excited state). A particular amount of energy is associated with a specific wavelength of light; the wavelength will be absorbed if this energy is able to make one of these electronic transitions as depicted in Figure 3-12. More energy is required for an electron to jump to a higher energy level, if the gap between the energy levels is larger; therefore, there will be light with a high frequency and shorter wavelength being absorbed. After the absorption of light, electronic excitation will occur for all molecules, but very high energy radiation (in a vacuum ultraviolet < 200 nm) is required for most of the molecules [60]. The following transitions depicted in Figure 3-13 show the absorption of light in the UV-Visible region:

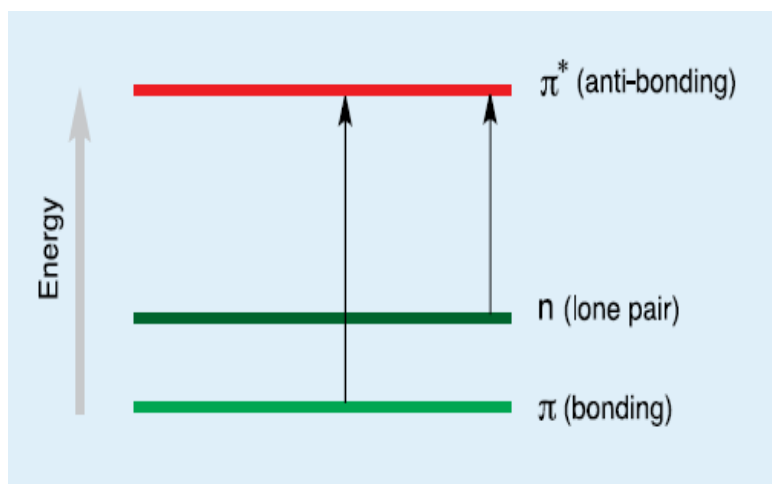


Figure 3-13: Electronic transition in the UV-Visible region [60].

In order for light to absorb in this region (200 – 800 nm, where the spectra are measured), the molecules must contain either σ bonds or atoms with non-bonding orbitals. A non-bonding orbital is a lone pair on oxygen, nitrogen or a halogen. [60].

3.4.5.2 Working principle of a UV-Vis spectrometer

A UV-Vis spectrometer is used to measure the intensity (absorbance) of ultraviolet and visible light that passes through a sample, measurements can either be done at a single wavelength or a scan can be performed over a range in the spectrum. The range of UV region is from 200 to 400 nm and the visible region ranges from 400 to 800 nm. The main components in a UV-Vis spectrometer are:

- Light source (provides radiation from 200 to 800 nm)
- Sample holder
- Monochromator (to separate different wavelengths of light)
- Detector

Figure 3-14 below shows a schematic representation a UV-Vis spectrometer

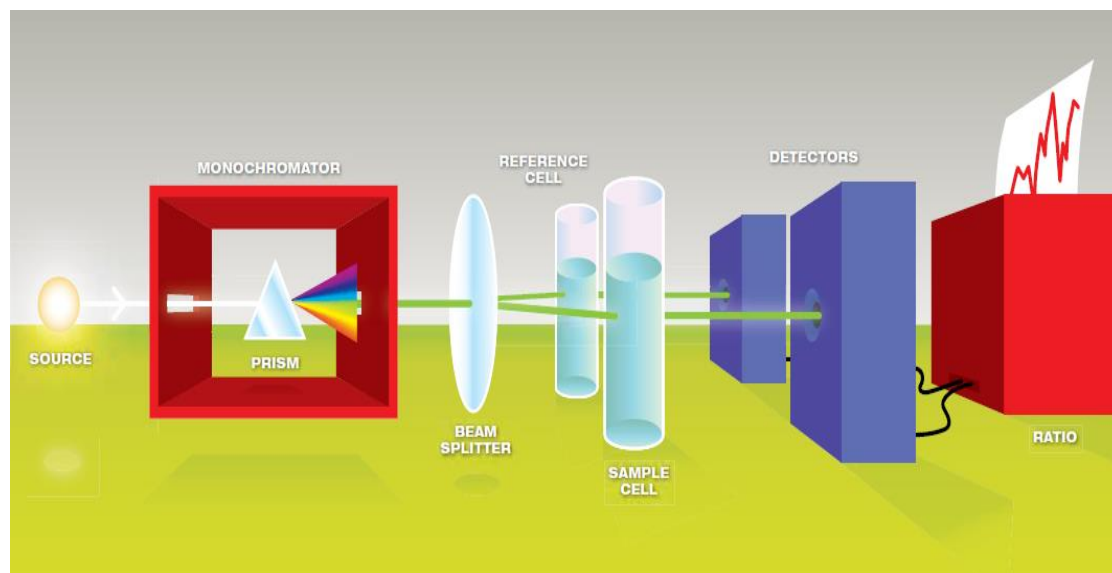


Figure 3-14: Schematic representation of a UV-Visible Spectrometer [60].

Light from the source is directed to a diffraction grating (prism like) where it is split into different wavelengths. The intensity of light that passes through a reference cell (I_0) and the sample cell (I) is measured for each wavelength. If $I < I_0$, it means that the sample has absorbed some of the light. According to the following equation, the absorbance (A) of the sample is related to I and I_0 :

$$A = \log_{10} \frac{I_0}{I} \quad 3-4$$

When the light reaches the detector it gets converted into a current, where the current is directly proportional to the intensity. The spectrum is then plotted as absorbance (dimensionless) against wavelength (nm) in the region of ultraviolet and visible light of the electromagnetic spectrum [60, 61]. UV-Vis results and discussions are in chapter 4.6. An overall decrease in the energy band gap

(E_g), and increases in the Urbach energy (E_u) and number of carbon cluster (N) are observed with increasing fluence.

3.4.6 Current-voltage measurements

When measuring resistances that are greater than $1\text{ G}\Omega$, instruments such as electrometer and picoammeter, voltage source are needed. High resistance measurements are done using an electrometer through either one of these two methods; the constant-voltage method (Figure 3-15 shows a configuration of the constant-voltage method) or constant-current method. The former uses an ammeter with a voltage source. An instrument that can measure low current and a constant DC voltage source is required so as to measure high resistance using the constant voltage method. Since the picoammeter has a voltage source, the unknown resistance can be measured automatically.

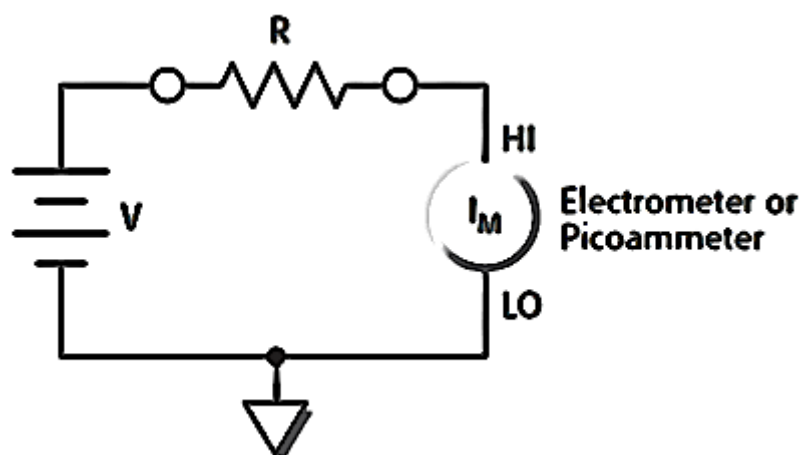


Figure 3-15: Constant voltage method for measuring high resistance [62].

In this method, the voltage source (V) is connected in series with the unknown resistance (R) and the ammeter (I_m). The voltage drop across the ammeter is negligible, therefore all the test voltage appears across R . The resistance is then calculated using Ohm's Law ($R = V/I$), while the current is determined by the ammeter. A resistance versus voltage curve can be developed by testing at selected voltages.

Measuring insulating resistance, testing two terminal high resistance devices and determining the volume and the surface resistivity of insulating materials are some of the applications that use the constant-voltage method.

The Keithley 6487 picoammeter with a voltage source was used to investigate the sheet resistance of irradiated and non-irradiated PET samples. The instrument was operated in the remote (REM) mode by connecting it to a personal computer (PC) through a RS-232 cable. An add-in utility for Microsoft Excel was installed in the PC for control of the picoammeter and for data acquisition. The information herein is given in reference [62]. The resistance of PET decreases with ion fluence while the current increases; detailed results on I-V measurements are found in chapter 4.7.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

Sample characterization results are reported in this chapter. The characterization of PET is done with the purpose to utilize them in semiconductor applications. Analysis of measurements performed and the discussion of these results are presented herein. All experiments and characterizations were performed on commercial PET/Mylar thin films supplied by Sigma-Aldrich. Implanted PET foils (thickness = 130 μ m) were all cryogenically cooled (using liquid nitrogen) and implanted with the following parameters:

- Energy = 100 keV
- Current density = 4 μ A/cm²

Titanium and argon ions were used for the implantation to various ion fluences, samples with fluences ranging from 2×10^{16} to 2×10^{17} cm⁻² are all implanted with Ti⁺ and Ar⁺ ions. All characterization techniques reported herein are on pristine and implanted PET thin film samples.

4.2 XRD

Generally, polymers contain both crystalline and amorphous regions [63]. For the changes in the crystalline properties of PET thin films, pristine and implanted samples were analysed for both argon and titanium ions. The XRD spectra for the pristine sample and implanted samples are shown in Figure 4-1 and Figure 4-2.

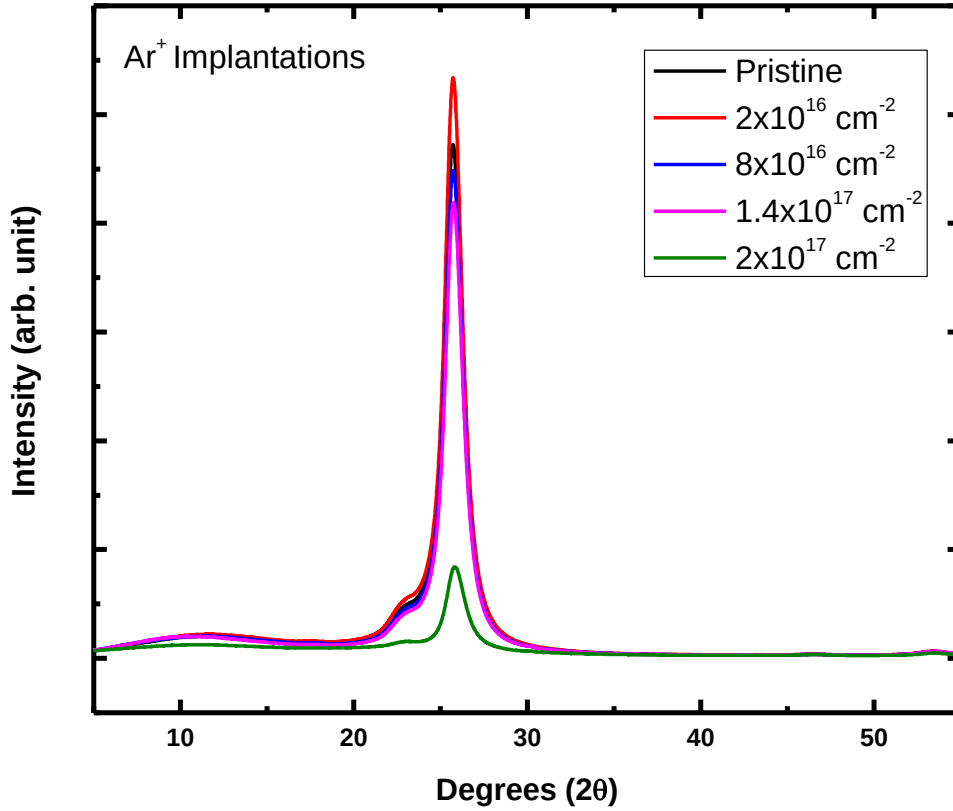


Figure 4-1: XRD spectra for pristine and irradiated PET using Ar⁺ ions at various fluences

The spectra indicate that all the PET samples are semi-crystalline in nature with the diffraction peak being at $2\theta \approx 25.727^\circ$ for the pristine sample. This peak corresponds to the (100) plane [64]. A change in the intensity of peaks has been observed with all implanted samples; with some showing an increase and others a decrease. There are small shifts in the 2θ positions of all peaks ranging from 25.719° to 25.872° ; these shifts are insignificant therefore indicating that ion implantation has no effects on the lattice parameter of the material. Small shifts in peak positions have been reported for PET implanted with 3 keV Ar⁺ ions for fluences of 10^{18} ions/cm² [65]. There is peak intensity increase for the sample implanted at 2×10^{16} ions/cm²; thereafter, peak intensity is observed to be undergoing a decrease with increase in fluence.

Figure 4-2 shows titanium implanted XRD diffraction peaks with one peak (8×10^{16} ions/cm²) having an intensity that is lower than the peak for the pristine sample. The three other peaks, $2 \times$

10^{16} , 1.4×10^{17} and 2×10^{17} ions/cm², have increased intensities. Increases and decreases in peak intensities, with increase in fluence at fluences ranging from 10^{10} to 10^{18} ions/cm² have been reported in some literature [63, 65]. The reason for this inconsistent behaviour has not yet been identified/reported.

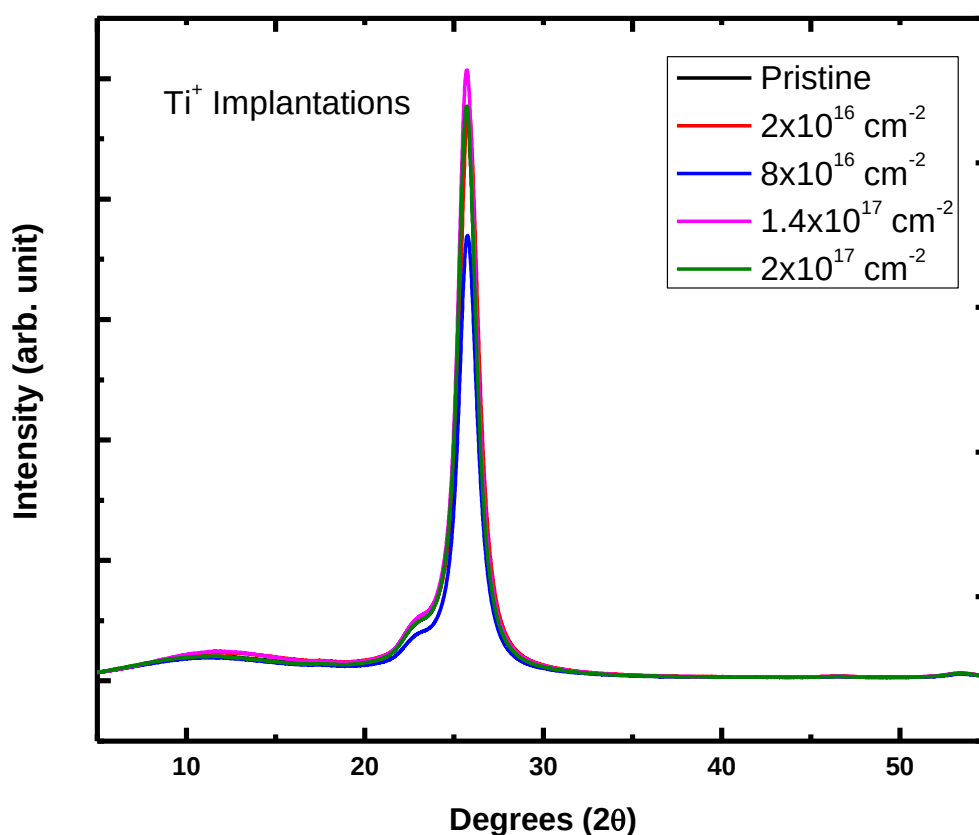


Figure 4-2: XRD spectra for pristine and irradiated PET using Ti⁺ ions at various fluences

The increased peak intensities indicate that the polymer material has undergone an enhancement in its crystallinity. Therefore, the decrease in intensity indicates that material has increased its amorphous nature, see full width at half maximum (FWHM) values in tables Table 4-1 and Table 4-2. This could be associated with degradation induced by implantation causing chain scission and

cross-linking which could lead to the disorder of the polymer matrix. Overall, there seems to be a decrease in the crystallinity of the samples implanted with titanium, whereas samples implanted with argon have undergone amorphization. Amorphization in PET matrix is further confirmed by UV-Vis results in chapter 4.6.

The crystallite size (D) was calculated using the Scherrer equation; this was done using the full width at half maxima (FWHM) that was obtained from the XRD spectra. The Scherrer equation is expressed as:

$$D = \frac{\lambda}{\beta \cos \theta}$$

where: D is the crystallite size,

$\lambda = 1.5418 \text{ \AA}$ and is the wavelength of the $\text{CuK}\alpha$ X-ray radiation,

β is the FWHM of the diffraction peak and

θ is the Bragg angle (rad)

Table 4-1: XRD parameters for the pristine and Ar^+ implanted PET films

Fluence (ions/cm ²)	Peak Position 2 Theta (deg.)	FWHM (deg.)	Crystallite Size D (nm)
Pristine	25.727	1.4980	6.042
2.0×10^{16}	25.742	1.4904	6.073
8.0×10^{16}	25.752	1.4759	6.103
1.4×10^{17}	25.768	1.4759	6.133
2.0×10^{17}	25.872	1.5755	5.746

Values of the FWHM and crystallite size are shown in Table 4-1 and Table 4-2. There is an inconsistent pattern in the sizes of the crystallite with fluence for samples implanted with argon. Samples implanted to 2×10^{16} and 2×10^{17} ions/cm² have smaller crystallite sizes from the pristine samples whereas samples implanted at 8×10^{16} and 1.4×10^{17} shows to have increased in size. Titanium implanted samples show a decrease in size for the sample implanted to the lowest fluence (2×10^{16} ion/cm²), from 6.042 for the pristine to 5.869 nm. The crystallite size then increases gradually with ion fluence but having one sample (2×10^{17} ion/cm²) with a crystallite size that is larger than the pristine sample. There has been an observed fluctuation in the crystallite sizes reported in [65] with increase in fluence. It has been reported that broadening of XRD peak indicates a decrease in crystallite size thereby resulting in the formation of disordered matrix in the material.

Table 4-2: XRD parameters for the pristine and Ti⁺ implanted PET films

Fluence (ions/cm ²)	Peak Position 2 Theta (deg.)	FWHM (deg.)	Crystallite Size D (nm)
Pristine	25.727	1.4980	6.042
2×10^{16}	25.821	1.5423	5.869
8×10^{16}	25.772	1.5029	6.023
1.4×10^{17}	25.730	1.4988	6.038
2×10^{17}	25.719	1.4882	6.082

4.3 SEM

The surface morphology of virgin and ion implanted PET samples are depicted in Figure 4-3 and Figure 4-4, EDX mapping of these samples are shown in Figure 4-5, Figure 4-7 and Figure 4-8. The pristine sample is smooth with no visible grains, meaning that the sample is transparent. The elemental composition of the pristine sample obtained via EDX shows composition of 74.3 wt.% for carbon and 25.7 wt.% for oxygen; this makes up 100% of the material composition. Hydrogen content cannot be detected by EDX; this is because the technique does not detect light elements below the atomic number 11 (Na). Although this is the case; some elements below this number are exceptions.

The SEM images for implanted PET samples show some developments of micro roughness on the surface after irradiation. Material damage due to ion implantation experienced by the polymer increases with ion fluence as expected.

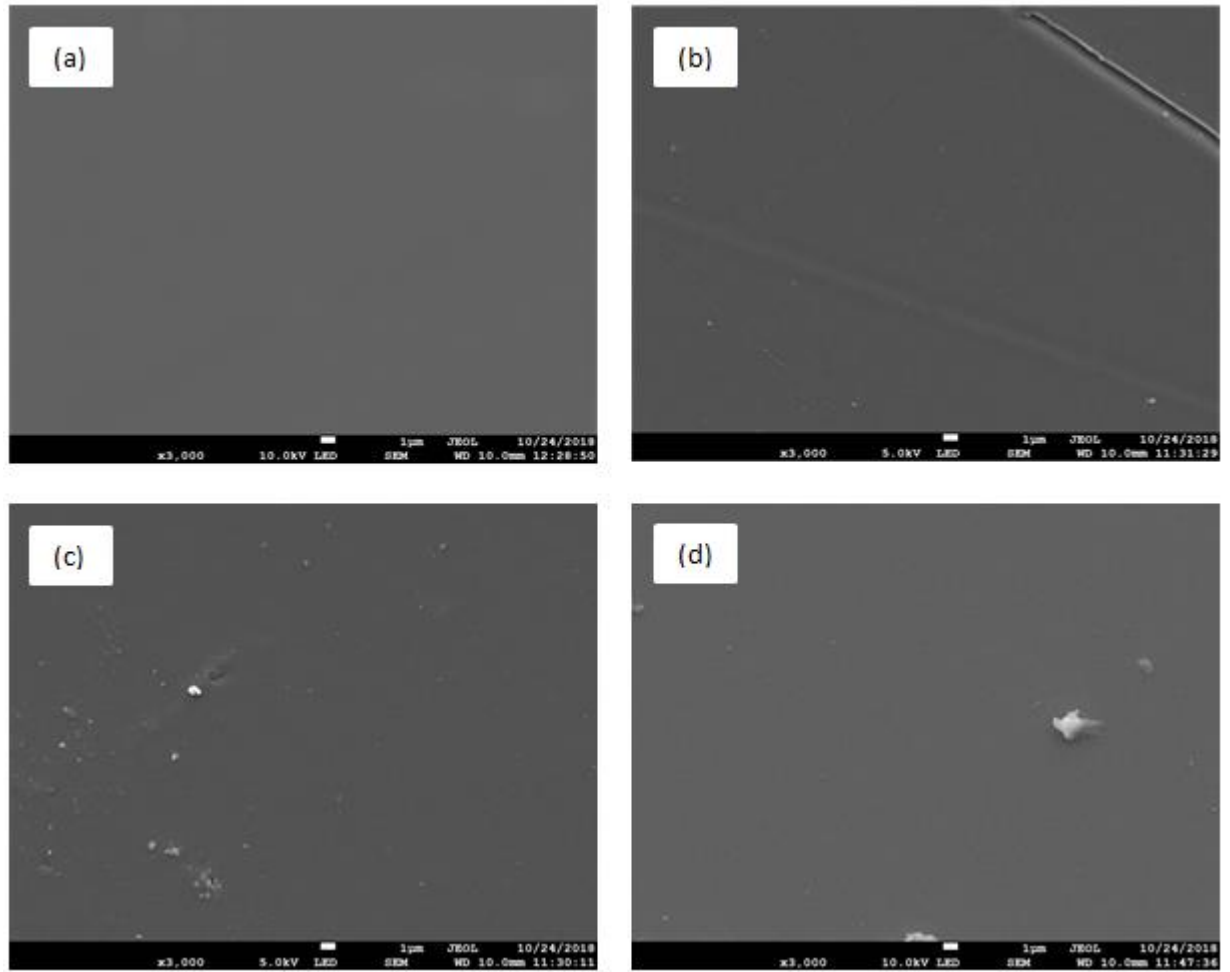


Figure 4-3: SEM micrographs for (a) pristine and irradiated PET films using Ar^+ ions at (b) 2×10^{16} , (c) 8×10^{16} and (d) 2×10^{17} ions/ cm^2

Figure 4-3 (b) is an image of PET implanted with argon at 2×10^{16} ion/ cm^2 , and it is observed that there are very few nano-granules that have formed. There is also what appears to be a “scratch” at the top right corner of the image, this could be due to mishandling of the sample during ion implantation and/or measurements leading to wear. The image in Figure 4-3 (c) shows an increase in the sizes of the granular structures that are observed in Figure 4-3 (b), and they seem to have also increased in number. There are a few voids observed on this sample. The highest Ar implanted sample, Figure 4-3 (d) seem to be a lot smoother, almost like the pristine. Sample with a very few granules that are a bit larger than previous samples.

The Ti^+ implanted samples have a similar trend, with the size and number of granules increasing with the Ti^+ ion fluence. The large features in Figure 4-4 (d) might not be related to the effects of ion irradiation but it could be wear debris/particles. Figure 4.4 (c) shows what appears to be hillocks on the surface. The formation of these hillocks indicates degradation in the PET matrix, leading to carbonaceous cluster formation.

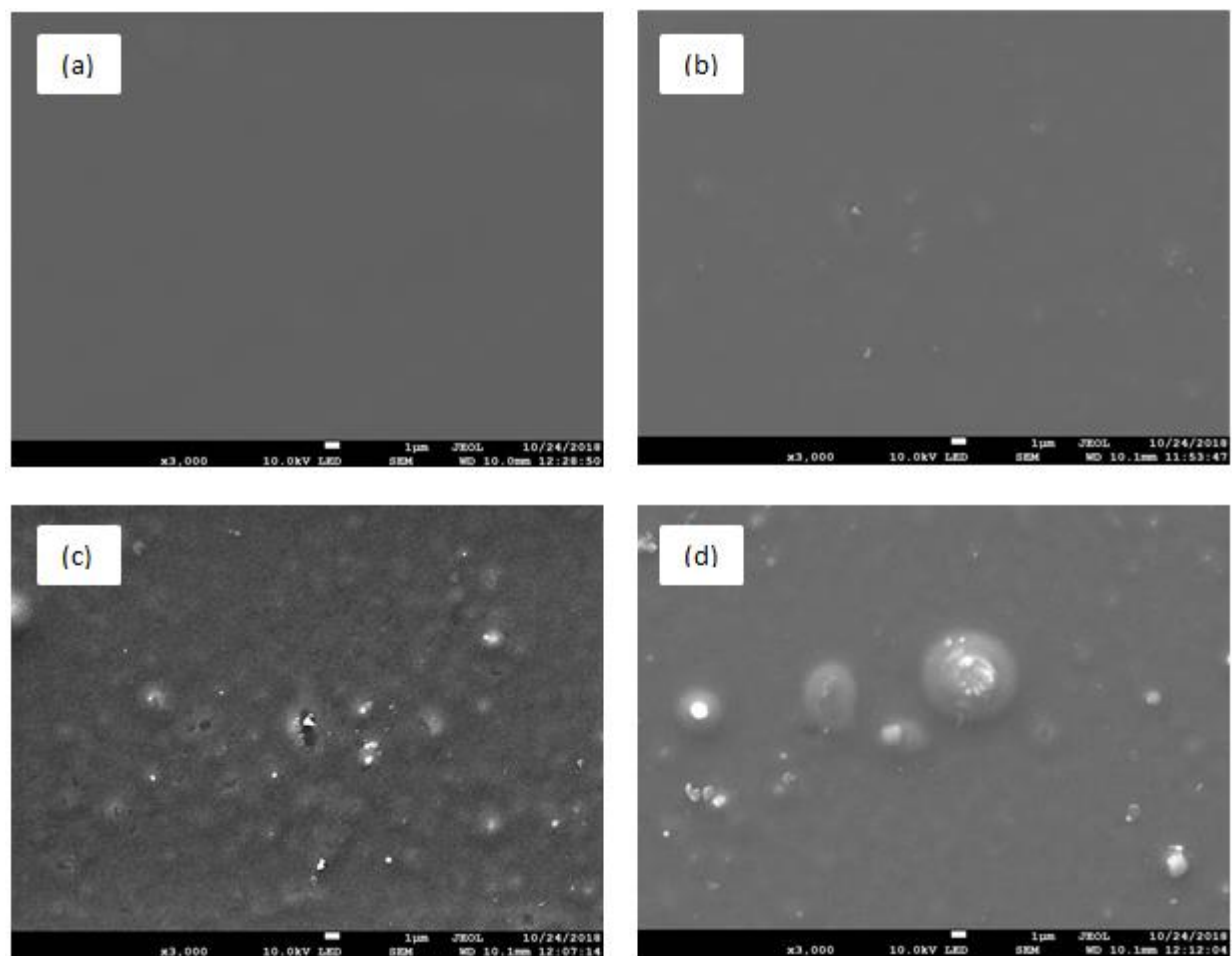


Figure 4-4: SEM micrographs for (a) Pristine and irradiated PET films using Ti^+ ions at (b) 2×10^{16} ions/cm², (c) 8×10^{16} ions/cm² and (d) 2×10^{17} ions/cm²

4.3.1 EDX

The EDX mapping shown in Figure 4-5 represents the pristine sample and it indicates that the material is truly virgin, with only carbon and oxygen being visible. The mapping of argon implanted samples shows traces of the element implanted in the matrix; this is shown in Figure 4-7. The sample implanted at $2 \times 10^{16} / \text{cm}^2$ shows a 0.5 wt% Ar element composition with an increase in the carbon content and a decrease in the oxygen content from the pristine sample, see Table 4-3. Figure 4-7 (b) shows the EDX mapping of PET thin film implanted at $2 \times 10^{17} / \text{cm}^2$. The implanted argon ions show a decline in the wt.%, from 0.5 to 0.3 from $2 \times 10^{16} / \text{cm}^2$ implanted sample, although the previous sample is implanted to a lower ion fluence. This could be due to the additional element detected by the instrument which is indium, and it comprises of 51.4 wt% of the entire composition of the material; the elemental composition in wt% of all samples are given in Table 4-3.

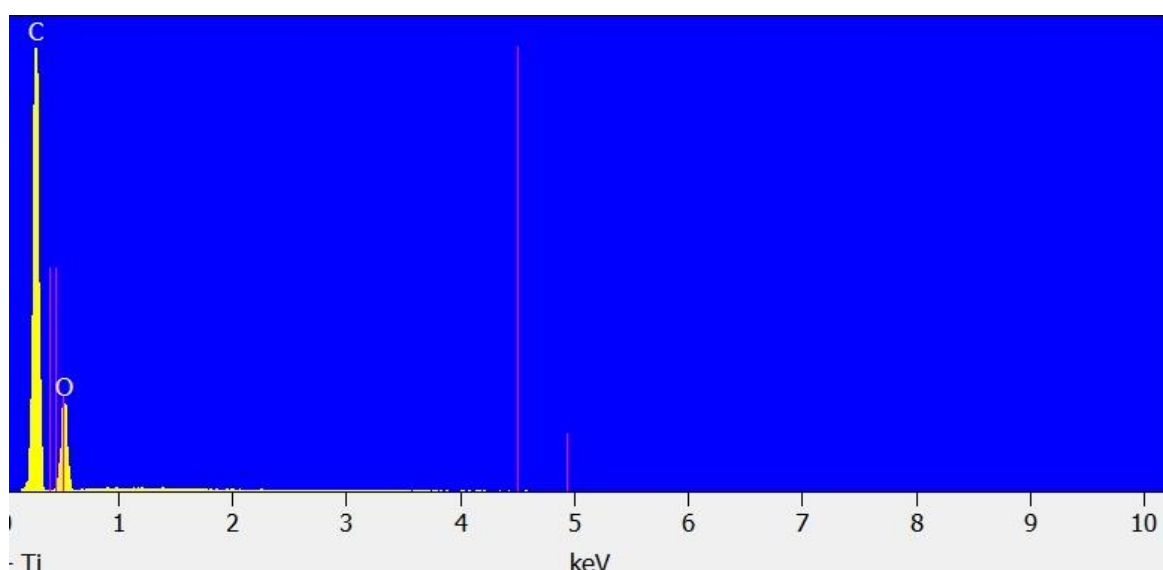


Figure 4-5: EDX mapping for pristine PET

The PET samples used in this study have an indium tin oxide (ITO) coated layer and their thickness is 130 μm , as depicted by in Figure 4-6. The mapping in Figure 4-7 (b) consists of more than 50%

of indium in the materials composition. EDX analyses material in depths ranging from 100 nm to 1 μm ; therefore, it could be that the implantation was performed on the ITO coated side. Another explanation is that the ion source of the ion implanter was not properly cleaned and therefore consisted of traces of indium from previous implantations/experiments. PET and ITO have very different surface resistivity values, a multimeter was used to measure the conductivity on each side to determine which side was the PET (not coated with ITO) so that implantation could be performed on the PET side. The difference was obvious, therefore it is not possible that the EDX instrument measured the ITO coated side, furthermore; there is no indication that the material has tin (Sn) which is an element found in ITO.

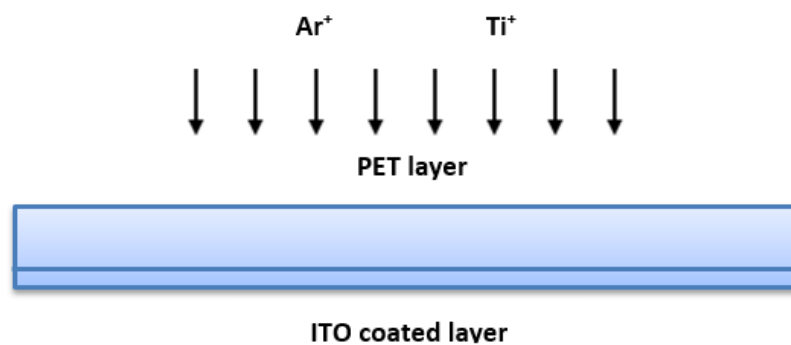


Figure 4-6: ITO coated PET thin film

The decrease in the argon content could be due to the rising indium content found in Figure 4-7 (b). The overall percentages in the carbon content show to have decreased and increased; and there is an overall decrease in oxygen contents. Lower fluence implanted samples in both ions have an increase in carbonisation while the higher fluence implanted samples have a decline in the C content. When observing both spectra in Figure 4-7, there is a noticeable difference in argon peaks. The peak in (a) is much smaller than the one in (b); thus indicating that the Ar

content in (b) is more than that in (a), this is the case since there are more ions implanted in (b) than there are in (a).

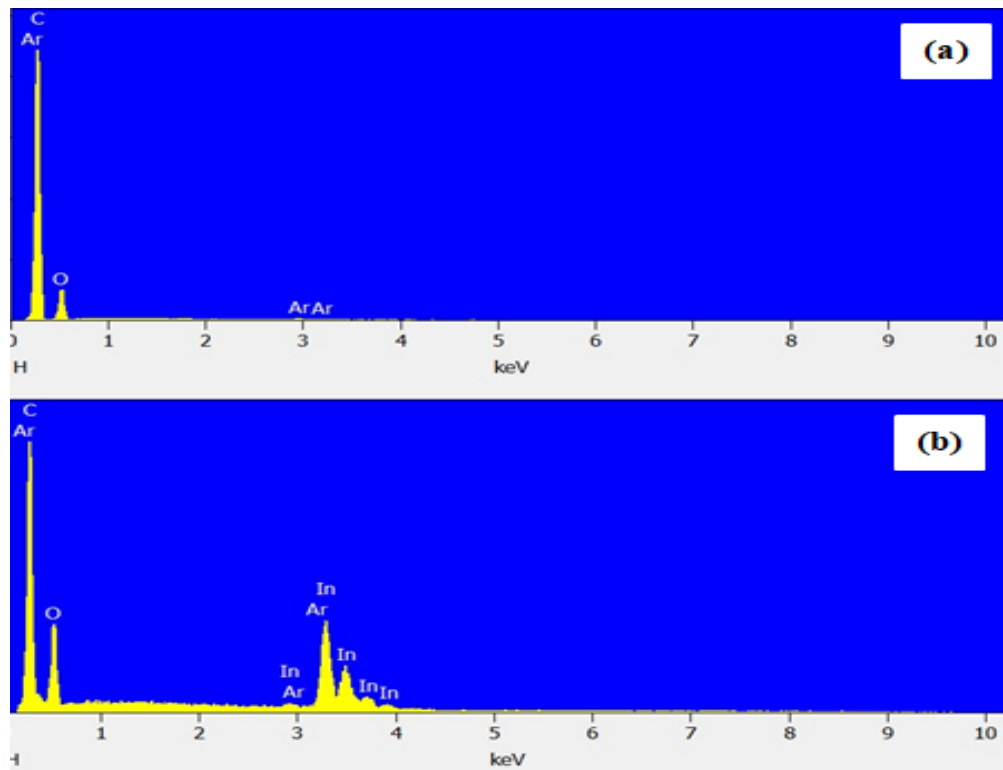


Figure 4-7: EDX mapping for argon implantations at fluences of (a) 2×10^{16} and (b) 2×10^{17} ions/cm²

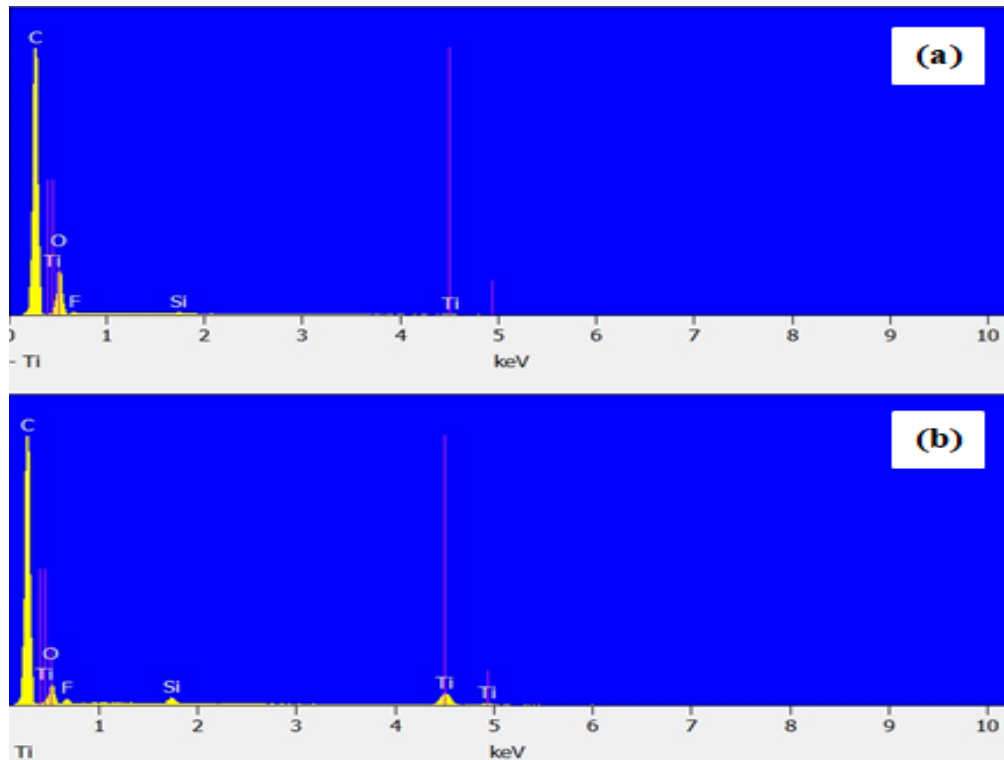


Figure 4-8: EDX mapping for titanium implantations at fluences of (a) 2×10^{16} and (b) 2×10^{17} ions/cm²

EDX spectra for titanium implanted at 2×10^{16} and 2×10^{17} /cm² are shown in Figure 4-8 (a) and (b) respectively. Both mappings show that there have been three new elements introduced into the PET matrix, two of which are not supposed to be contained in the material as they were not implanted and do not make up the virgin material, these are fluorine (F) and silicon (Si). Since there is no fluorine and silicon in ITO, it is then certain that implantations and measurements were performed on the uncoated side. Justifications of the two materials being present is that of the sample holder having residue from previous implantations; it should also be noted that the samples were coated with graphite in a centrifugal instrument before the SEM measurements were performed, this was done to prevent “charging” during measurements since PET is an insulator. Most materials are coated with graphite prior to measurement, and some of those materials are

powders, it is therefore possible that there was some residue from those materials in the instrument that got into contact with the film.

Table 4-3: Elemental composition of pristine and ion implanted PET samples.

Element weight (wt%)	Pristine	Argon		Titanium	
		$2 \times 10^{16} \text{ cm}^{-2}$	$2 \times 10^{17} \text{ cm}^{-2}$	$2 \times 10^{16} \text{ cm}^{-2}$	$2 \times 10^{17} \text{ cm}^{-2}$
Carbon	74.3	82.4	30.1	74.9	69.0
Oxygen	25.7	17.1	18.1	21.4	9.6
Argon	-	0.5	0.3	-	-
Titanium	-	-	-	0.6	16.7
Fluorine	-	-	-	2.7	3.6
Indium	-	-	51.4	-	-
Silicon	-	-	-	0.4	1.0

There are traces of titanium, fluorine and silicon detected in both spectra of Figure 4-8, in (a) there are small - almost nonvisible peaks of the elements while (b) gives a better, more visible view of these peaks; this indicates an increase in the contents of these elements with increasing ion fluence and it is confirmed by data provided in Table 4-3.

The composition of carbon increases by 0.6 wt% and that of oxygen decreases by 4.3wt% from the pristine to $2 \times 10^{16} / \text{cm}^2$ implanted Ti^+ ions. The decrease in the content of O allows for the development of Ti with 0.6 weight %, F with 2.7 wt% and Si with 0.4 wt%. The elemental contents of Ti, F and Si increases for sample implanted at $2 \times 10^{17} / \text{cm}^2$; C and O decrease at this fluence. Ti content increases by 16.1%. Ar content increases to 0.5 wt% for sample implanted to $2 \times 10^{16} / \text{cm}^2$ then decreases 0.3 wt% for samples implanted to $2 \times 10^{16} / \text{cm}^2$.

4.4 HI-ERDA

Depth profiling of pristine sample depicted in Figure 4-9: Depth profiles of pristine PET shows the elements contained in PET. There seems to be a relationship between the spectra of carbon and hydrogen; in depths where there is an increase in C, a decrease in H is observed and vice versa. This relationship is observed in all samples, unimplanted and implanted. The reason for this trend could be due to an uneven distribution of the two elements throughout the film.

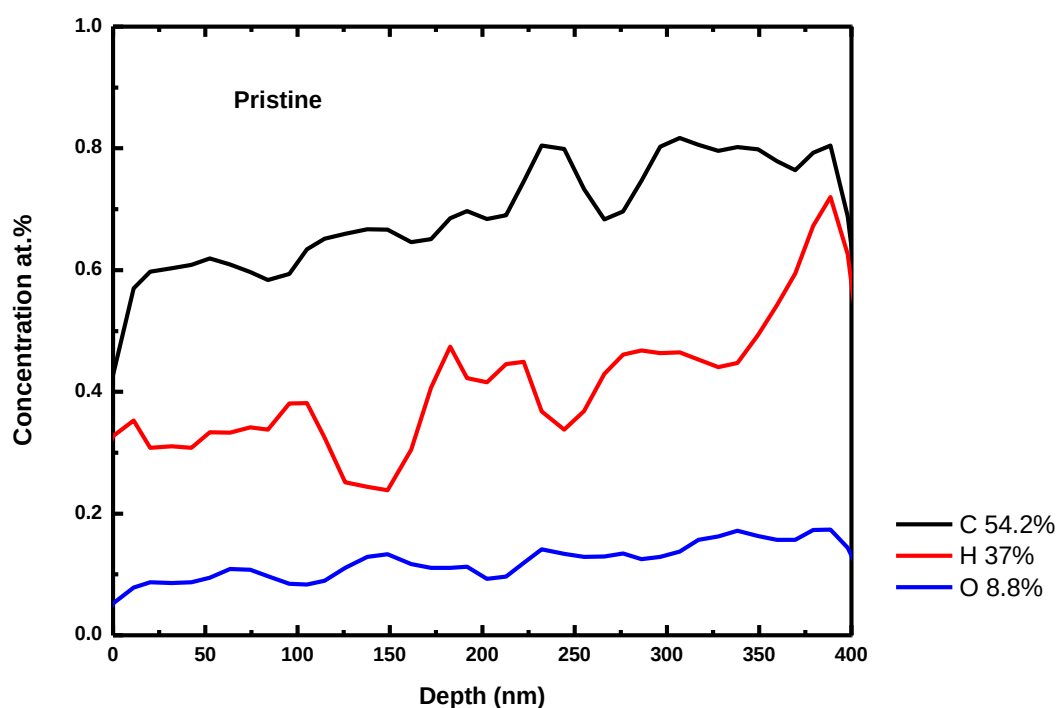


Figure 4-9: Depth profiles of pristine PET

The effects of ion implantation cause carbonization in polymers. There is an overall increase in the carbon concentration after irradiation with both argon and titanium, this is due to bond breakage and cross-linking resulting in aromatic growth/carbon clusters. The increase in C is accompanied by a decrease in the H and O concentrations. This decrease is a result of the liberation

of hydrogen and oxygen gases in the subsurface layer of PET. These effects are due to nuclear stopping interactions.

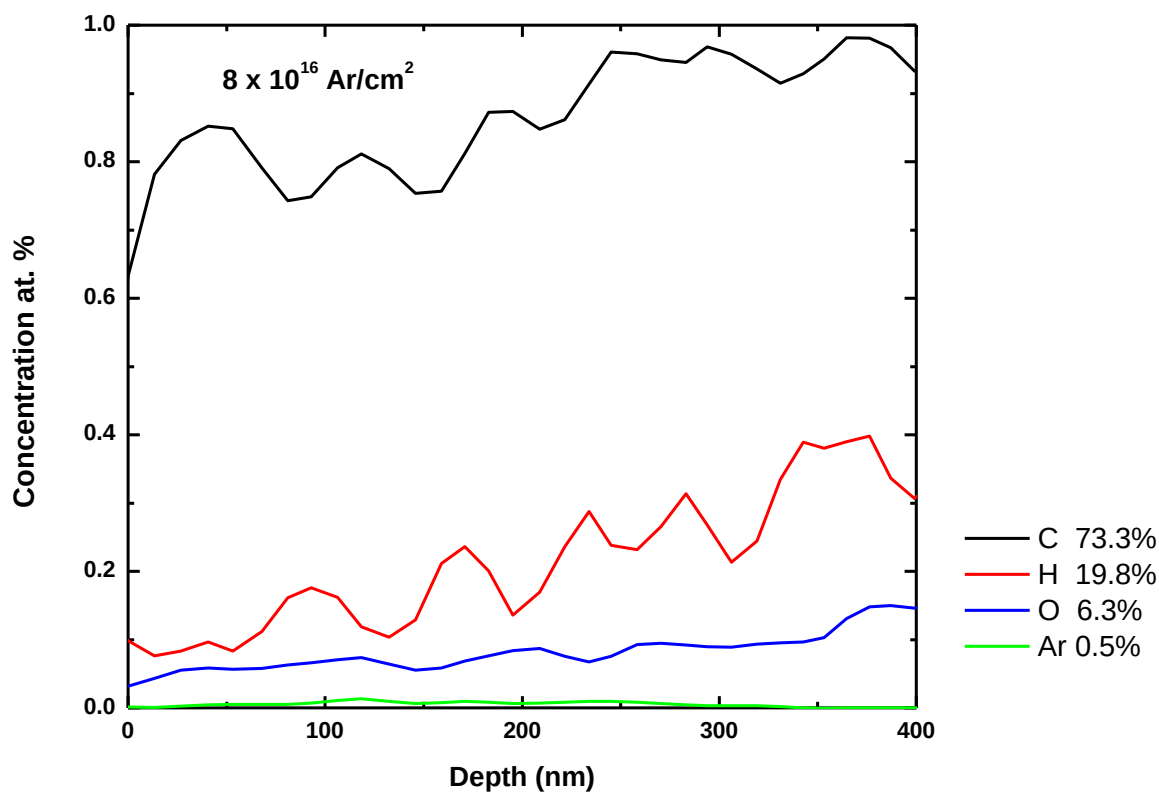


Figure 4-10: Depth distribution of argon implanted PET at $8 \times 10^{16} / \text{cm}^2$

Figure 4-10 and Figure 4-11 represent argon implantations in the PET films and they show Ar profiles to be flat; this means that the ions have diffused and are therefore distributed on the bulk of the surface region thus escaping from the PET film. Effects of diffusion have been reported to be significant on light species polymer distribution [6], the effect is common in inert gases implanted at high fluences ($>10^{16} / \text{cm}^2$). This could be the reason that the content of Ar for both fluences are no more than 1 wt%. There is a decrease in the concentration of Ar ions with an increase in ion fluence which suggests that the higher the fluence, the greater the diffusion escape of the gas atoms from the surface.

Although argon ions are distributed along the surface region, SRIM simulation predicts that the projected range of 100 keV Ar ions in PET is 137 nm. In some instances, like this one, simulated predictions differ greatly from experimentally obtained data.

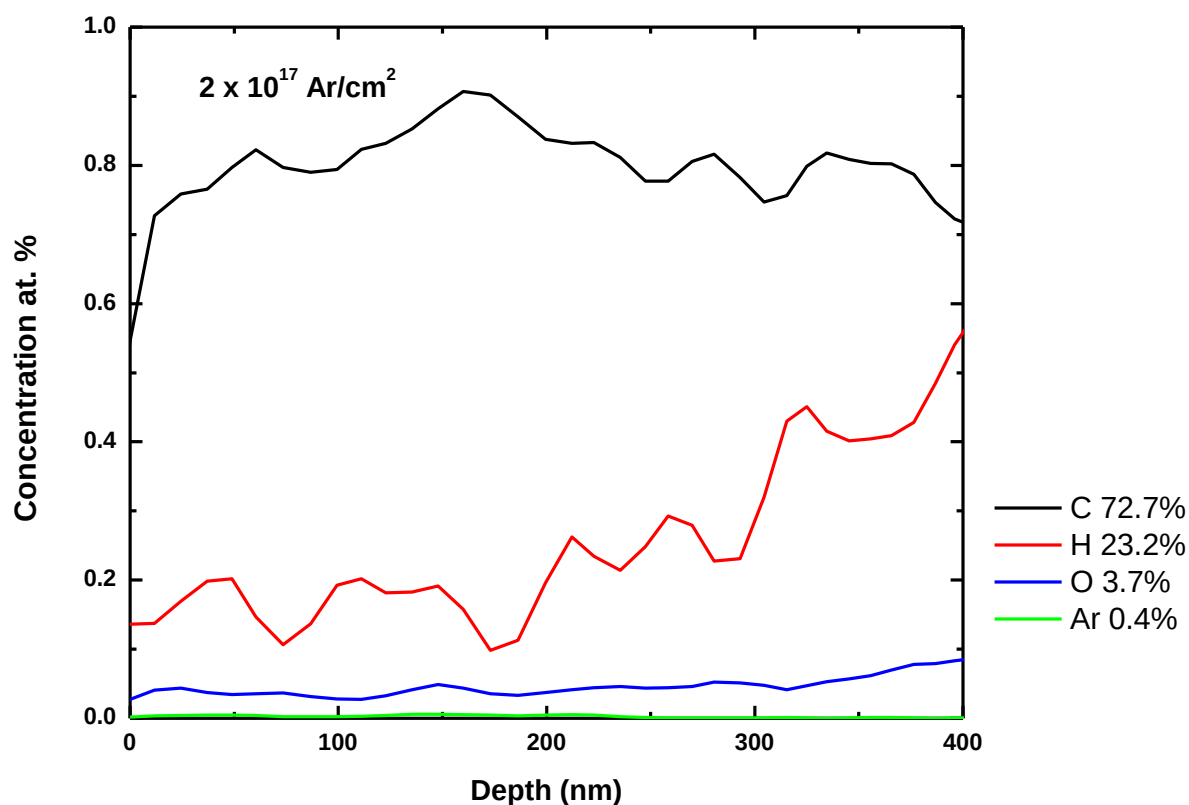


Figure 4-11: Depth distribution of argon implanted PET at $2 \times 10^{17} / \text{cm}^2$

The profiles for titanium shown in Figure 4-12 shows an accumulation of the Ti ions between 70 and 200 nm. The SRIM simulation prediction of 100 keV Ti ions implanted in PET give an R_p of 127 nm; therefore, the experimental data in figures Figure 3-2 and Figure 3-3 is confirmed by SRIM. This accumulation could be due to formation of Ti-O phases in the implantation region resulting in nucleation and this renders the Ti ions less mobile compared to the inert Ar. Metal clusters are a result of the low interaction energy between the metal and polymer causing an accumulation.

Oxygen concentrations decrease more with Ar ion while hydrogen decreases more with Ti. O concentrations are higher in Ti implanted samples; this could be contributing to Ti-O phase formation. It is observed in Figure 4-12 and Figure 4-13 that the accumulation of Ti results in lower degree in carbonization - Ti ions displace C-atoms in these regions.

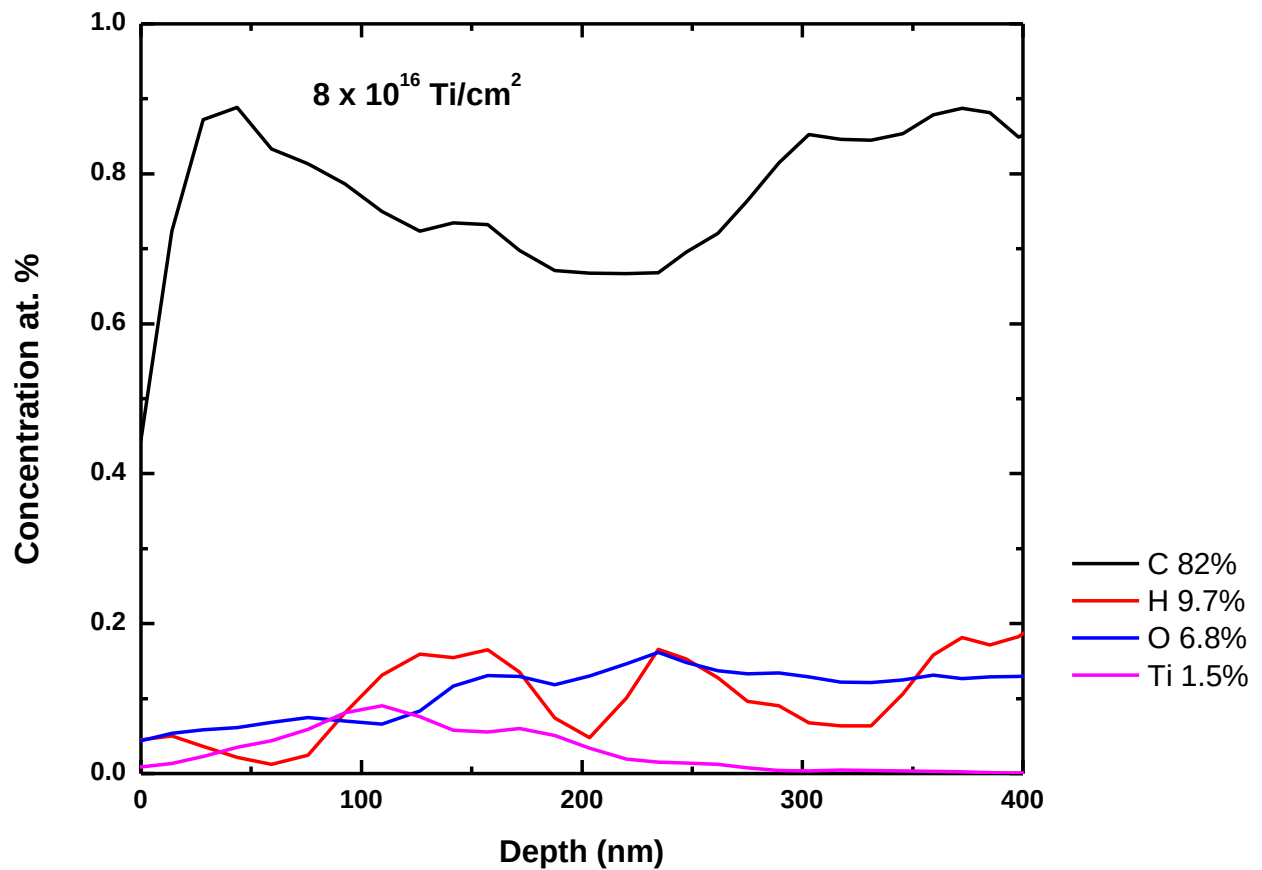


Figure 4-12: Depth distribution of titanium implanted PET at $8 \times 10^{16} /\text{cm}^2$

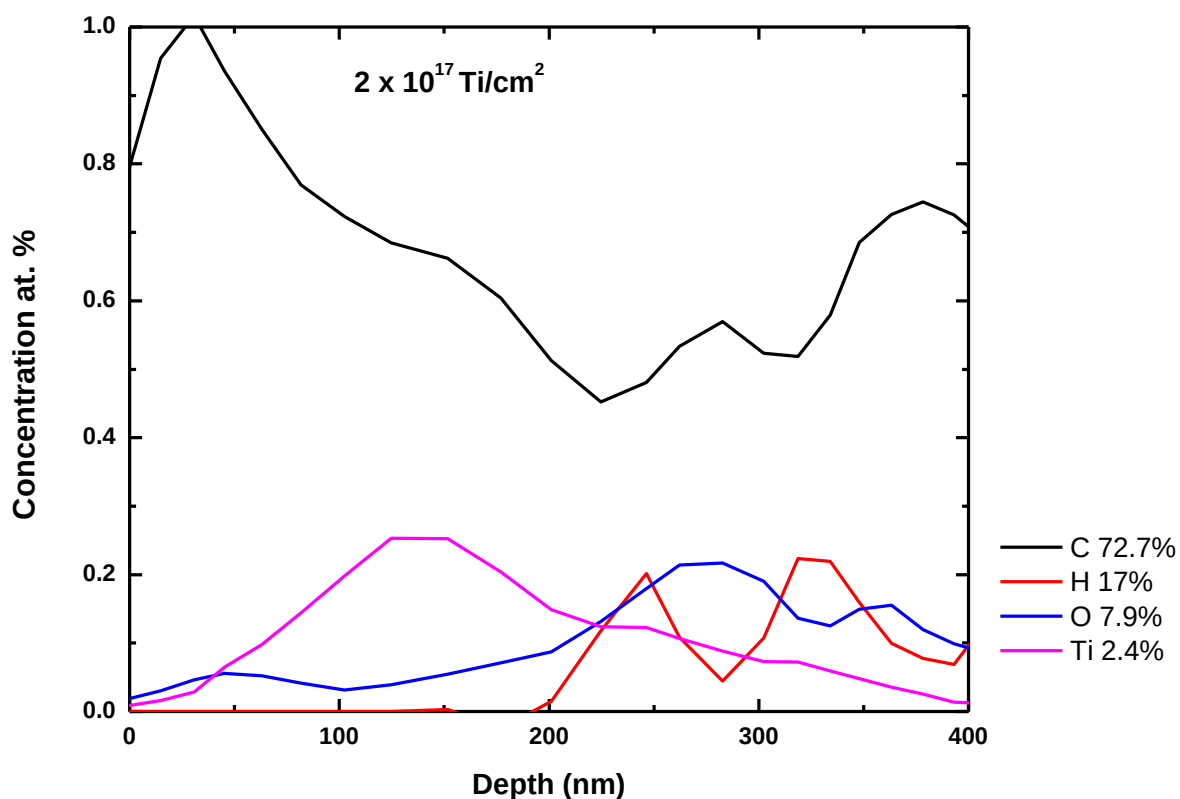


Figure 4-13: Depth distribution of titanium implanted PET at $2 \times 10^{17} / \text{cm}^2$

4.5 FTIR

Polyethylene terephthalate has the formula $\text{C}_{10}\text{H}_8\text{O}_4$ which clearly indicates that it consists of carbon, hydrogen and oxygen groups and is an infrared active material with characteristic absorption peaks [64]. The structural formula shown below suggests that the polymer contains a benzene structure, a carbonyl group (in the red box representing an ester) and ether.

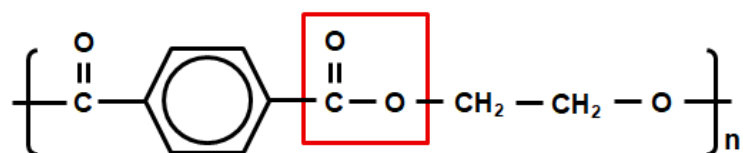


Figure 4-14: PET structure [64]

Although characteristic peaks increase and decrease in intensity after irradiation, there is an overall decrease with increase in ion fluence with most peaks disappearing at the highest fluence of implantation. This is attributed to the degradation in polymeric material. There is also increase and decrease in absorbance of some samples. These are associated with functional groups that are present in the PET matrix. Slight shifts in peak positions denote a change in bond strength; bonds associated with functional groups can either be weakened or strengthened by this change. When an absorption peak shifts to a lower wavelength the bond weakens, therefore it gets strengthened when it shifts to a higher wavelength [64]. Figure 4-15 and Figure 4-16 represent FTIR spectra of pristine and argon and titanium irradiated samples. Formation of new absorption peaks is not observed with all implanted samples but there are slight shifts in the position of some peaks to shorter wavelengths.

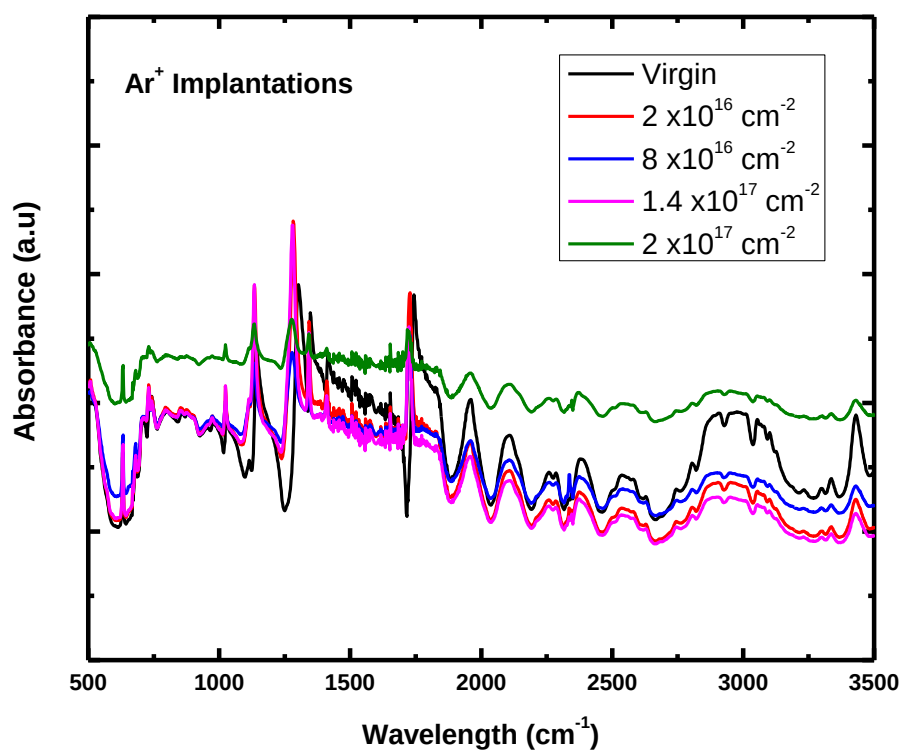


Figure 4-15: FTIR spectra for virgin and irradiated PET using Ar^+ ions at various fluences

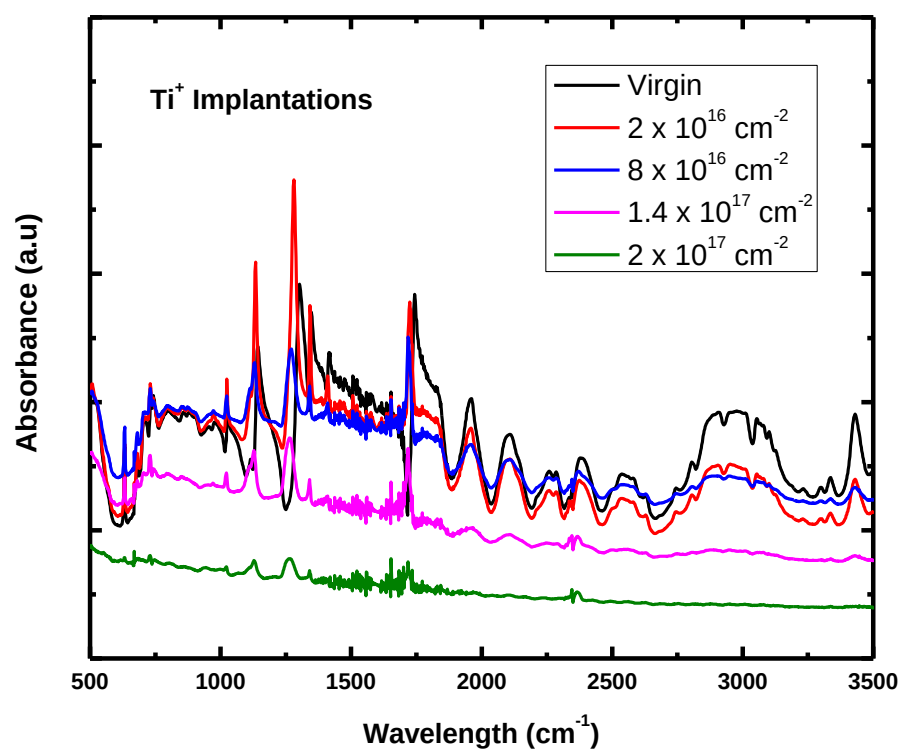


Figure 4-16: FTIR spectra for virgin and irradiated PET using Ti^+ ions at various fluences

4.5.1 Discussion

Figure 4-15 shows the relationship between virgin and Ar⁺ implanted samples. There is an increase in the absorbance for samples implanted to 2×10^{16} and 8×10^{16} ions/cm². The absorbance of these two samples decreases from the wavelength of >1300 cm⁻¹. These samples show a very similar trend in the decrease and increase in both the absorbance and intensity of peaks.

Figure 4-16 shows the relationship between virgin and Ti⁺ implanted samples. The results show a consistent trend on the overall absorbance of the samples which show a decrease with increasing ion fluence. Both ions show a similar trend when it comes to the samples implanted at 2×10^{16} , 8×10^{16} and 1.4×10^{17} ions/cm² where there is a slight increase in absorbance for the samples implanted to the lowest fluence. The absorbance further increases for the second lowest implanted samples (8×10^{16} /cm²), but it decreases for the samples implanted at 1.4×10^{17} . For the samples implanted to 2×10^{17} , by Ar⁺ there is a significant increase in absorbance from the previous sample whereas there is a significant decrease when it comes to Ti⁺. The absorbance and intensity of peaks gradually decreases with increase in fluence. It is also observed that there are slight shifts in the wavelength of peaks for both ions.

There is an unidentified peak that is observed at 632 cm⁻¹ for the pristine sample. C-H bending modes are the most dominant in all the samples, these are observed in the wave number ranging from $680 - 977$ cm⁻¹ and are associated with alkene and aromatic groups. A broad peak at 710 cm⁻¹ is attributed to CH₂ bending mode of an alkane group. The C-O stretching modes in alkoxy ester and acyl ester have characteristic peaks at wavelengths 1026 and 1348 cm⁻¹ respectively. The absorption peak at 1142 cm⁻¹ corresponds to C-O-C stretching in ether. Aromatic ester appears at 1301 cm⁻¹ which is attributed to O=C-O-C stretching mode. The characteristic peak at 1744 cm⁻¹ corresponds to C=O in the carbonyl group of an ester. In the range 1957 to 2560 cm⁻¹ there are a few unidentified peaks that are observed, these peaks are consistent with most of the samples. A

very broad peak is observed in the range of 2744 to 3229 cm^{-1} and this is assigned to O-H stretching in carboxylic acid, this pattern overlaps the C-H stretching modes. Two weak peaks appear at 3301 and 3335 cm^{-1} and a medium peak at 3430 cm^{-1} ; these are attributed to O-H stretching modes in alcohol.

The absorption peak at 680 cm^{-1} is attributed to a C-H bend of an alkene group; there's no change in its position but there is a small decrease in its intensity. The decrease in intensity and disappearance of peaks corresponding to C-H bonds have been reported [16, 66]. Peaks at 732 and 742 cm^{-1} represent mono-substituted benzene rings and 797 cm^{-1} corresponds to para-substituted benzene rings; no significant changes in the position is observed, but peak intensity decrease with fluence where peaks disappear for samples irradiated at higher doses in both argon and titanium. In literature [65], the para-substituted benzene rings are observed at 873 cm^{-1} and decrease with implantation fluence. The broad peak (710 cm^{-1}) decreases in intensity with increase in fluence until it completely disappears, the loss in peak intensity signifies a destruction of the alkane bonds. There is not much difference with peaks at 954 and 977 cm^{-1} when it comes to samples implanted with Ar, but a gradual decrease in peaks intensities is observed until they completely disappear at the highest fluence. With Ti there is a noticeable decrease in peak intensity from the lowest implanted sample to the highest where there are no peaks at all. Absorption peaks at 1026 and 1342 cm^{-1} which are C-O stretching correspond to alkoxy ether and acyl ester respectively, slightly shifted to lower wavenumbers with intensities showing initial increase then decrease with fluence with significant decrease when it comes to Ti implanted samples. The C-O band is reported to lie at 972 cm^{-1} [65], and undergoes a decrease with increase in fluence. The peaks 1142 (C-O-C in ether) and 1301 cm^{-1} (O=C-O-C in aromatic ester) are among the strongest peaks and show the most prominent changes where the absorption peaks shifted to lower wavenumbers 1134 – 1128 cm^{-1} and 1283 – 1263 cm^{-1} respectively with increase in fluence, therefore there is a weakening of bonds or chain scission. Both peaks show an increase in intensity at lower fluences and decreased

at higher fluences. The peak representing the C=O carbonyl group at 1744 cm^{-1} (saturated) is a strong peak and it shifts to $1728 - 1718\text{ cm}^{-1}$ and becomes unsaturated. The intensity of this peak decreases with increasing ion fluence and it is hardly recognizable with the sample implanted with Ti at $2 \times 10^{17}/\text{cm}^2$. A decrease in intensity of this band after implantation is reported to be situated at 1714 cm^{-1} [16]. The unidentified peaks in the region of 1957 to 2560 cm^{-1} have a decrease in intensities with increasing fluence until they disappear. Absorption peaks corresponding to O-H stretching show a decrease in the absorbance of the peaks with fluence, however the absorbance increase for the sample implanted with argon at the highest fluence (2×10^{17} ions/ cm^2). These peaks have disappeared with samples implanted in titanium at 1.4×10^{17} and $2 \times 10^{17}\text{ cm}^{-2}$.

The absorption bands at 850 , 973 and 1472 cm^{-1} are reported to correspond to the trans-configuration of ethylene glycol in PET. These bands are associated with crystallinity of PET with crystallographic plane (100). A decrease in absorbance is reported to be associated to the decrease in crystallinity [64, 67]. For the pristine PET sample; there is no visible peak observed at 1472 cm^{-1} , the peak closest to 973 cm^{-1} is at 977 cm^{-1} and 850 cm^{-1} is at 859 cm^{-1} . These bands show a decrease in absorbance when it comes to titanium implanted samples but an increase for samples implanted with argon, this could be due to the predicted projected range by SRIM – 100 keV argon ions are predicted to penetrate deeper than titanium ion in PET.

A comparison for both ions was made for each one of the four ion fluences used to implant the PET thin films. Figure 4-17 shows a comparison for implantation done at a) 2×10^{16} and b) 8×10^{16} ions/ cm^2 . It is observed in Figure 4-17 (a) that there are minor differences in the spectra and these are only associated to the absorbance of the samples. The samples implanted with titanium shows a slightly increased absorbance than argon. Figure 4-17 (b) shows that samples have little to no differences, but there are significant changes in the intensity of peaks from spectra in (a) especially with regards to strong peaks (1142 , 1301 and 1744 cm^{-1}). Figure 4-18 (a) shows a

comparison between Ar and Ti at fluences of 1.4×10^{17} ions/cm²; the spectra show a significant variation. The spectra of Ar implanted PET has a higher absorbance and peak intensities are much higher than the Ti implanted sample, there are also slight variations in the peak positions; Ti peaks have shifted to lower wavenumbers. This indicated that the polymer has experienced more degradation when it comes to Ti than Ar. Also there seems to be a higher intensity in peak intensity for argon from Figure 4-18 (b). The Ti implanted sample has drastic decrease in peak intensity where some peaks have disappeared, the degradation of the PET film could be the reason for this observations.

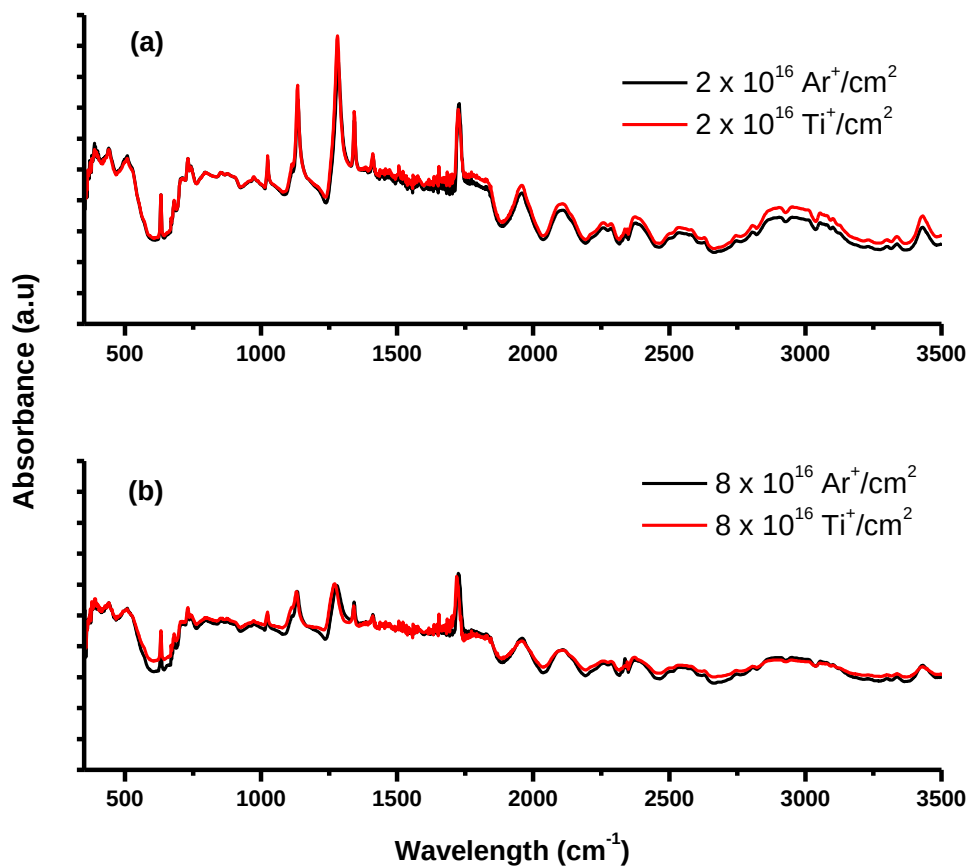


Figure 4-17: FTIR spectra for argon and titanium implanted PET (a) at fluences of 2×10^{16} ions/cm² and (b) 8×10^{16} ions/cm²

Figure 4-18 (b) show samples implanted at 2×10^{17} ions/cm², compared to the other fluences these two samples have a greater absorbance difference with argon having higher absorbance. Peak intensity has decreased significantly, with most peaks disappearing for titanium implanted sample. This decrease is associated with the decrease in the functional group corresponding to the peak.

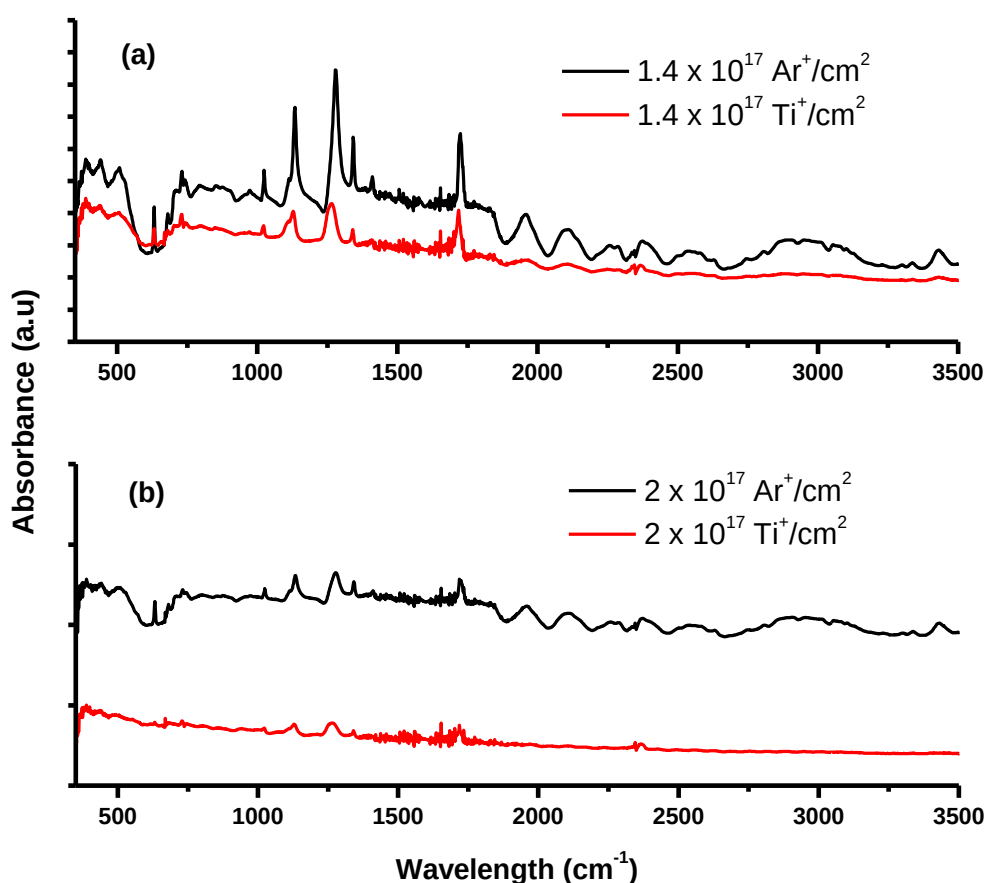


Figure 4-18: FTIR spectra for argon and titanium implanted PET (a) at fluences of 1.4×10^{17} ions/cm² and (b) 2×10^{17} ions/cm²

The FTIR results show that there has been material degradation in the polymer matrix with peak intensities decreasing with fluence. Drastic decreases are observed for samples implanted with Ti

where most peaks have completely disappeared with the sample implanted to $2 \times 10^{17} / \text{cm}^2$. There is also peak disappearance with Ar implanted PET but not as significant as Ti implanted PET. Bonds have been weakened as observed from the peak positions shifting to lower wavenumbers, with major shifts observed for absorption bands corresponding to ester and ether functional groups in the range 1142 to 1744 cm^{-1} .

4.6 UV-Vis absorption spectroscopy

The optical absorption spectra for virgin and implanted PET foils were performed in the wavelength range between 300 and 800 nm .

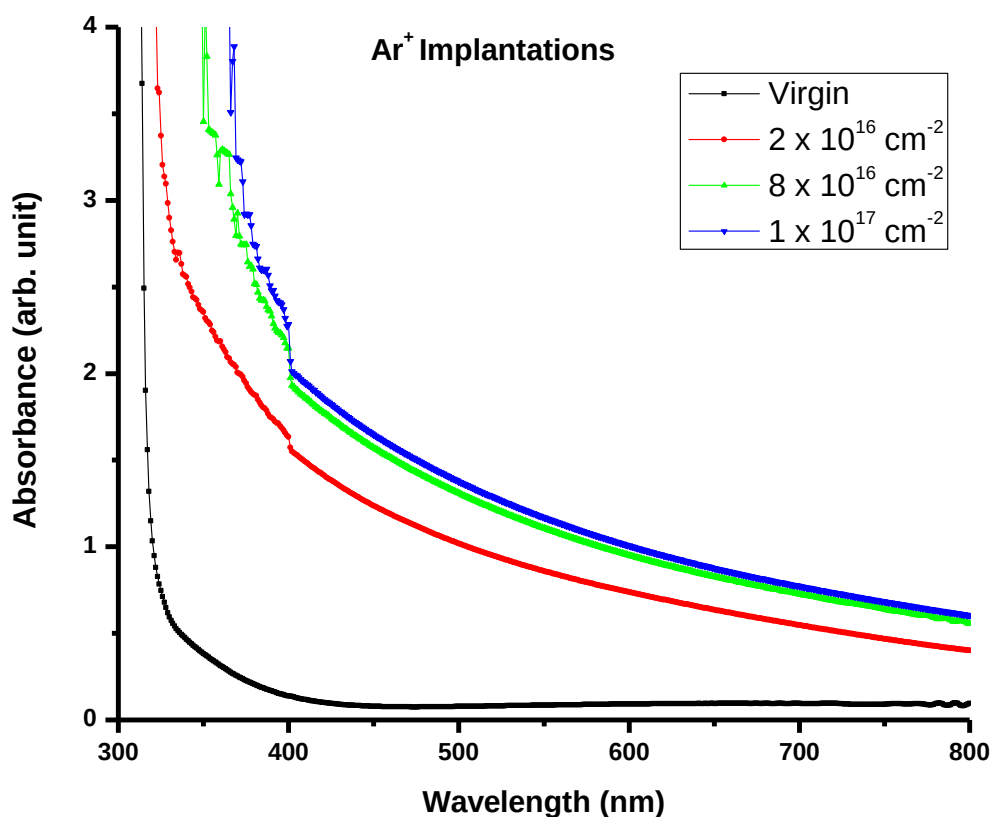


Figure 4-19: UV-Vis absorbance spectra for virgin and implanted PET sample using Ar⁺ ions

Figure 4-19 and Figure 4-20 show the optical spectra for pristine PET and after argon and titanium implantations respectively. With regards to the unimplanted sample, as the wavelength increases; a decrease in the absorption up to 438 nm is observed. For wavelength greater than 438 nm there is a continuous plateau region [65] in the visible region of the spectrum, where the sample is almost transparent [16]. After ion implantation for both Ar^+ and Ti^+ implantations there is an observed increase in absorbance due to a shift in the absorption edge towards higher wavelengths (red shift) [63, 65]. A red shift has also been reported in PET samples irradiated with gamma rays [64]. There is further shift with increasing ion fluence. This behaviour is characteristic of disorder induced by ion bombardment in the PET matrix causing cross-linking, chain scission, bond breakage, formation of carbon clusters etc. The intensity of the optical absorption increases as a result of ion beam irradiation [65].

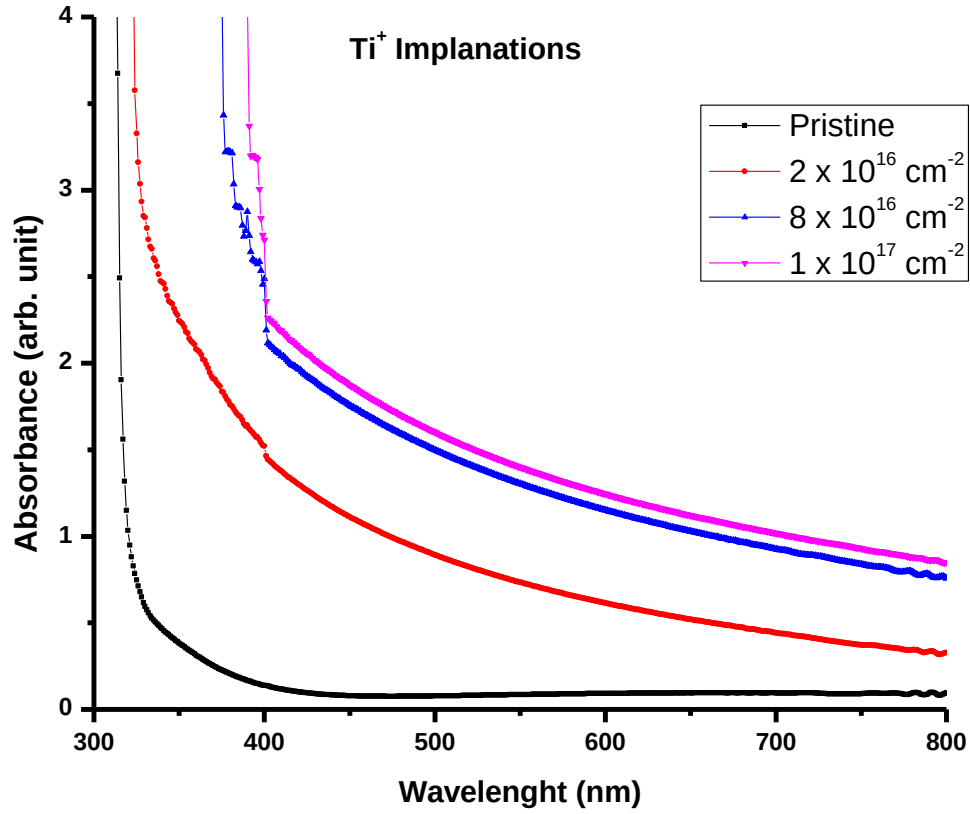


Figure 4-20: UV-Vis absorbance spectra for virgin and implanted PET sample using Ti^+ ions

4.6.1 Optical energy band gap

In general, it has been observed that there is a decrease in the optical band gap (E_g) in implanted PET sample as a result of carbon cluster network formation. Tauc relation is used to determine E_g , and it is an illustration of the variation of the absorption edge vs. photon energy, it is expressed as:

$$(\alpha h\nu) = \beta(h\nu - E_g)^n \quad (4-1)$$

where α is the absorption coefficient, β is a constant, h is Planck's constant, ν is the frequency and n is the index and can either be $1/2$, 2 , $3/2$ or 3 which represent direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively [13, 65, 68, 69, 70]. The transfer of electrons is vertical, from the top of the valence band to the bottom of the conduction band in

the allowed direct transition and here there is no change in momentum. The index in this case has a value of 1/2 for direct transition. In the forbidden transition, the transfer is non-vertical [71].

The estimation of the optical band gap is obtained by extrapolating the linear part of the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (extrapolation is not shown herein). The value is then obtained from the photon energy axis where the linear fit intercepts. The optical band gap values for pristine and implanted PET samples are given in Table 4-4 below. As observed in Table 4-4, the optical band gap decreases with increasing ion fluence. The value for pristine PET is 3.551 eV and it decreases to 2.007 eV and 1.843 eV for Ar and Ti ions at the highest fluence ($\phi = 1 \times 10^{17}$) respectively. The E_g value for Ar is relatively greater at this fluence as compared to Ti. The optical band gap for the pristine PET samples reported in literature [16, 63, 65, 66] range between 3.14 to 3.95 eV, and decreases to values between 1.48 to 3.05 for the fluence range 10^{12} to $10^{18}/\text{cm}^2$. Sun et al. reported a 2.67 eV band gap value for virgin PET, the E_g decreases to 0.78 for 120 keV Ar^+ , 0.51 for 240 keV Ar^{2+} and 0.38 for 360 keV Ar^{3+} implanted at $10^{16}/\text{cm}^2$. The relationship between the E_g and the ion fluence for both ions is shown in Figure 4-22 and discussed in section 4.6.4.

4.6.2 Urbach energy

The Urbach energy (E_u) defines irregularities (free radicals, saturated bonds, etc.) caused by ion irradiation in an implanted matrix. E_u is the width of the tail of localized states in the forbidden band gap (activation energy). It is assumed that the spectral dependence (low photon energy range) of the absorption edge follows the empirical Urbach rule:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (4-2)$$

where α_0 is a constant. E_u is determined from the linear relation between $\ln(\alpha)$ vs. photon energy $h\nu$ and the reciprocal of the slope of the linear fit gives the Urbach energy. Urbach energy values are given in Table 4-4.

An increase in the Urbach energy is observed with increase in fluence. From 0.449 eV for the pristine PET; E_u increases to 1.565 eV and 1.724 eV for Ar and Ti implanted PET respectively at $\phi = 1 \times 10^{17} / \text{cm}^2$. The Urbach energy values reported in Chawla et al. show an increase with fluence, from 0.29 eV for the pristine sample to 3.70 eV for the sample implanted at $1 \times 10^{17} / \text{cm}^2$ implanted with 200 keV Ar^+ ions. The Urbach energy values reported in this work show an increase with fluence, with the pristine samples having a value of 0.449 eV to 1.565 (Ar) and 1.724 eV(Ti) for the fluence $1 \times 10^{17} / \text{cm}^2$.

Table 4-4: Optical band gap estimated from Tauc plot, activation energy estimated from Urbach rule and number of carbon atoms in a cluster

Fluence (ions/cm ²)	Optical energy band gap E_g (eV)		Urbach energy E_u (eV)		No. of carbon clusters (N)	
	Ar	Ti	Ar	Ti	Ar	Ti
Pristine	3.551		0.449		94	
2×10^{16}	2.898	3.155	1.412	1.031	141	119
8×10^{16}	2.099	1.906	1.481	1.572	269	326
1×10^{17}	2.007	1.843	1.565	1.724	294	348

4.6.3 Carbon cluster network

The number of carbon clusters is closely related to the E_g and can be estimated from the Tauc relation:

$$E_g = \frac{34.4}{\sqrt{N}} \quad (4-3)$$

where 2β gives the band structure energy of a pair of adjacent π sites, with β being the resonance integral having a value of 2.9 eV (Hückel theory) [6]. N is the number of benzene rings forming in a cluster. From the equation it is clear that N can be determined from the optical band gap. N is indirectly proportional to E_g , and it is known that the E_g decreases with increasing ion fluence therefore N should increase with increasing fluence. This is apparent from the number of atoms in a cluster values given in Table 4-4. The increase in N is attributed to the graphitization of the polymer matrix after ion irradiation [66]. The number of carbon cluster formations reported in [65] increases from 119 (pristine) to 126 for low energy (3 keV) Ar^+ ions at $10^{18}/\text{cm}^2$. For 200 keV Ar^+ ions implanted at $10^{17}/\text{cm}^2$ reported in literature [66] the number of carbon clusters increases to 537. Therefore, the results obtained in this work is within the expected range.

4.6.4 Discussion

A comparison between metal (Ti) and non-metal (Ar) ions is shown by the use of UV-Vis plot depicted in Figure 4-21. The pristine sample is compared to each ion at different fluences in Figure 4-19 showing Ar implantations and Figure 4-20 showing Ti implantation. There is a clear observation of an increase in the absorbance towards the visible region of the spectrum with increasing fluence. The trend is the same with all the implanted samples irrespective of the ion.

Plot (a) in Figure 4-21 shows Ti implanted samples at $\phi = 2 \times 10^{16}$ which exhibits the least absorbance of all the implanted samples. Plots (b), (c) and (d) denote Ar implantations at 2×10^{16} ,

8×10^{16} and $1 \times 10^{17}/\text{cm}^2$ fluences respectively. With Ar implantations there is an almost constant increase in the absorbance with increasing fluence. Ti samples at 8×10^{16} and 1×10^{17} are represented by (e) and (f) respectively which shows the highest absorbance. Although (d) has a higher fluence than (e), it has a lower absorbance than (e). This could be due to the fact that (e) is a titanium implanted sample and since Ti is a metal and has a higher conductivity than argon, there is greater metal nanoparticles (NPs) production within the insulating PET matrix. It is also observed that the absorbance of (b) is greater than that of (a) even though both samples are implanted with the same fluence. This could be due to less interaction between the projectile metal ions with the PET sample thereby resulting in lower absorbance. The high absorbance in Ti implanted samples can also be explained in terms of the surface plasmon resonance (SPR) which is associated with the collective oscillation of free electrons in metal NPs [65].

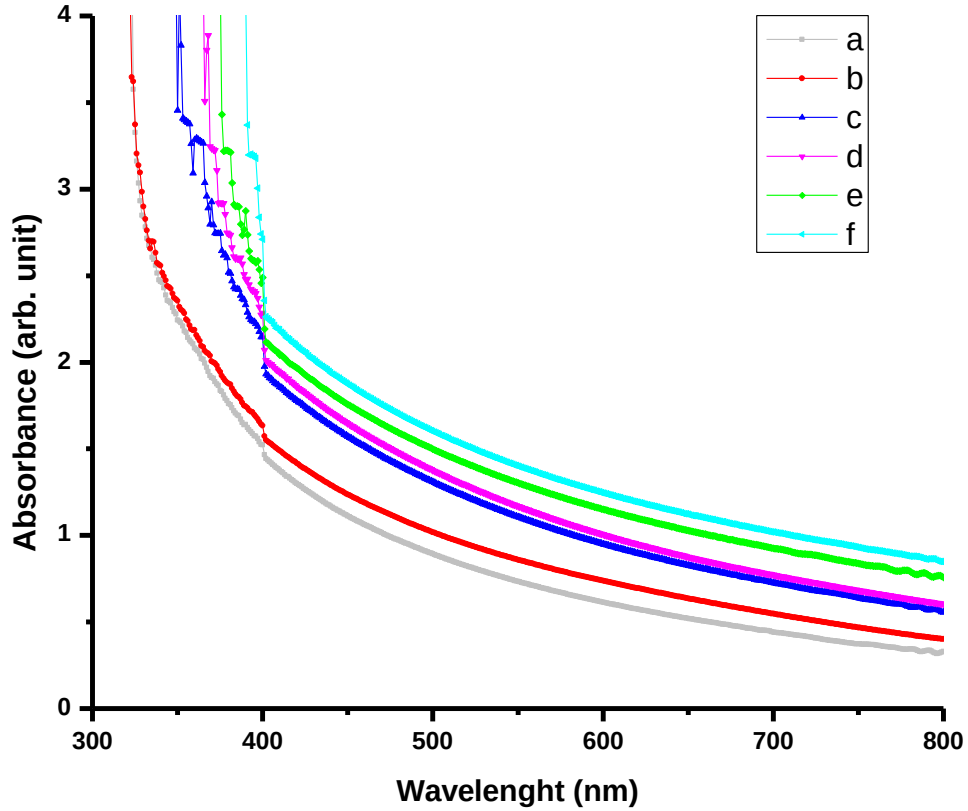


Figure 4-21: UV-Vis absorbance spectra for implanted PET at fluences of (a) $2 \times 10^{16} \text{ Ti}^+/\text{cm}^2$, (b) $2 \times 10^{16} \text{ Ar}^+/\text{cm}^2$, (c) $8 \times 10^{16} \text{ Ar}^+/\text{cm}^2$, (d) $1 \times 10^{17} \text{ Ar}^+/\text{cm}^2$, (e) $8 \times 10^{16} \text{ Ti}^+/\text{cm}^2$ and (f) $1 \times 10^{17} \text{ Ti}^+/\text{cm}^2$ implantations.

The observations in the optical spectra are correlated by the values of the optical band gap, Urbach energy and the number of carbon clusters given in Table 4-4. The values for Ti at 2×10^{16} are either highest or lowest (highest in terms of E_g and lowest in terms of E_u and N).

Figure 4-22 shows the relationship between ion fluence and optical band gap of Ar and Ti. In the figure it is observed that there is a decrease in E_g with increasing fluence. In both cases there is a drastic decrease between samples implanted with 2×10^{16} and $8 \times 10^{16} \text{ ions}/\text{cm}^2$; thereafter there is almost a saturation level/less difference (especially in Ti) between samples implanted with $8 \times$

10^{16} and 1×10^{17} ions/cm². E_g for Ti decreases from 3.155 eV (2×10^{16} /cm²) to 1.843 eV (1×10^{17} /cm²) and from 2.898 eV (2×10^{16} /cm²) to 2.007 eV (1×10^{17} /cm²) for Ar.

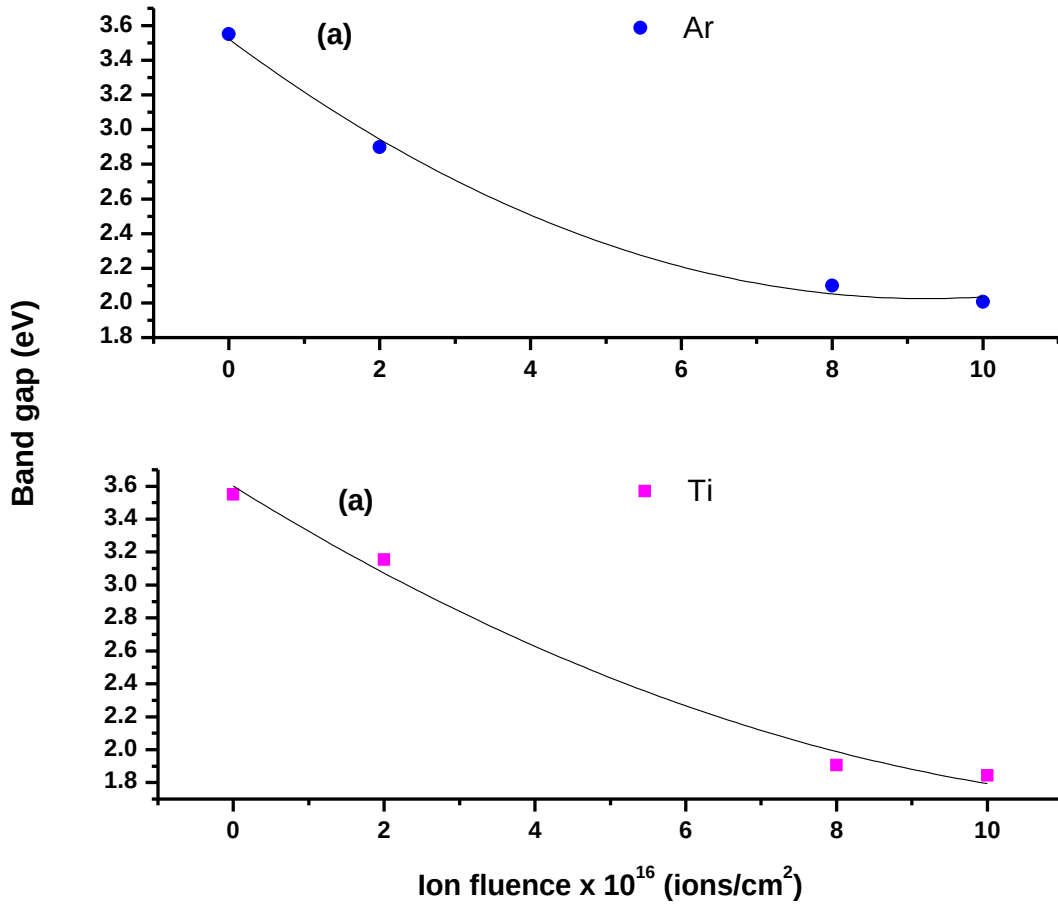


Figure 4-22: Plot of ion fluence versus optical energy band gap for (a) Ar⁺ and (b) Ti⁺ implantations

The increase in the Urbach energy and the number of carbon clusters/NPs with increasing fluence is associated with the damage caused by ion irradiation on PET. Carbon clusters increase to 348 (Ti) and 294 (Ar) at 1×10^{17} /cm² from 94 for the pristine sample. Ti at 2×10^{16} /cm² has the smallest number of carbon clusters formed in the PET matrix as compared to other implanted samples; this is also corroborated by the Urbach energy where the sample has the least amount of

irregularities with $E_u = 1.031\text{eV}$. Again, Ti at $8 \times 10^{16}/\text{cm}^2$ has more clusters formed than Ar at $1 \times 10^{17}/\text{cm}^2$, and it of course has a higher E_u with a value of 1.572 eV and 1.565 eV for Ar. The E_u of the pristine sample is 0.449 eV.

4.7 I-V measurements

The I-V curves for pristine and implanted PET samples are shown in Figure 4-23 and Figure 4-24. The characteristic curves were measured in the voltage range between 0 and 10 volts (V). There is an increase in current with increasing ion fluence; this increase is denoted by an increase in the number of carbonaceous clusters which form conductive paths and conjugated double bonds [65].

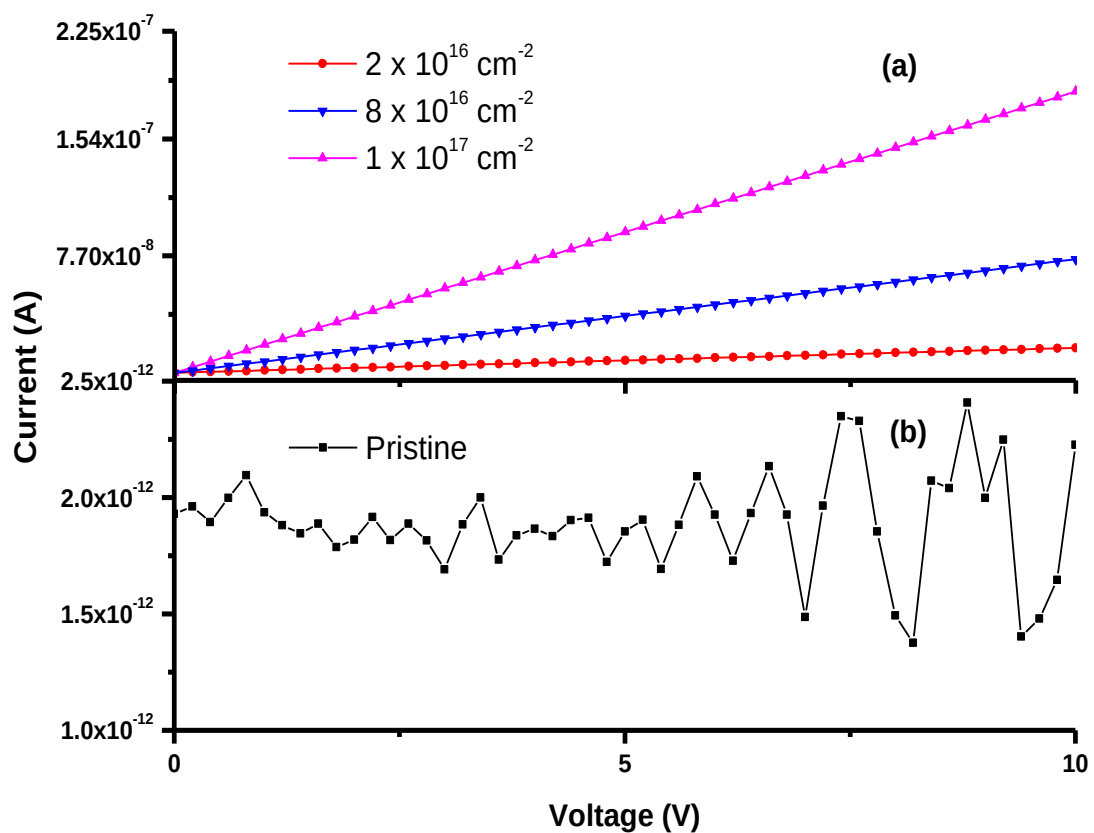


Figure 4-23: I-V characteristics of (a) Ar^+ implanted and (b) pristine PET samples

As observed in Figure 4-23 and Figure 4-24 the pristine PET sample shows a noise signal, this is because the measurement instrument used is a Keithley 6487 picoammeter. Picoammeters measure current in the range of nA (10^{-9}) and pA (10^{-12}) and virgin PET is an insulator that has a surface/sheet resistivity (R) value of the order $10^{13} \Omega/\text{sq}$. To determine the current, Ohm's law is used for two voltage values, $V = 1 \text{ V}$ and $V=10 \text{ V}$:

$$I = \frac{V}{R} = \frac{1}{10^{13}} = 10^{-13} \quad \text{and} \quad I = \frac{V}{R} = \frac{10}{10^{13}} = 10^{-12} \quad (4-4)$$

With such a small current ($<10^{-12}$), the instrument does not recognise the sample as having any electrical conductance.

Figure 4-23 and Figure 4-24 show the I-V characteristics of Ar and Ti implanted PET samples. There is an increase in current with an increase in voltage in both cases. There is a greater increase in current with increase in ion fluence. The relationship between I-V is linear and has a positive slope. From Ohm's law:

$$V = IR$$

V and I represent the x and y axis respectively, when the equation is written as:

$$I = \frac{1}{R} V$$

R is therefore the inverse of m (slope from the straight line equation: $y = mx + c$). Therefore, the resistance of the implanted PET samples by Ar and Ti ions in the range 2×10^{16} to $1 \times 10^{17} / \text{cm}^2$ can be determined.

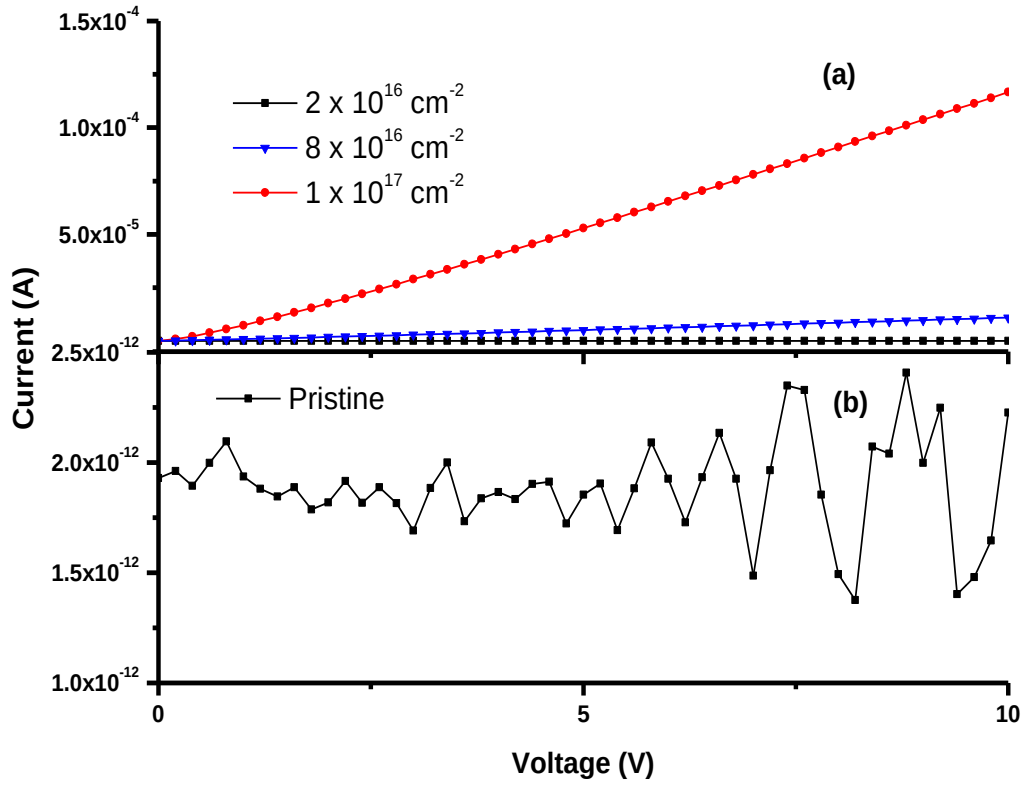


Figure 4-24: I-V characteristics of (a) Ti^+ implanted and (b) pristine PET samples

4.7.1 Discussion

Implanted PET samples shown present the same behaviour from both ions as observed in Figure 4-23 and Figure 4-24. At zero volts, all implanted samples have the same current, as the voltage is applied; a linear increase is observed in the characteristic curve. Samples implanted to higher fluences have a greater increase in the current and thus enhancing the conductance and decreasing the resistance. The samples implanted to fluences of $1 \times 10^{17} / \text{cm}^2$ at 10 V have current in the order 10^{-7} for Ar^+ and 10^{-4} for Ti^+ . Table 4-5 shows resistance and current values for the implanted samples at 10 volts.

Table 4-5: Current and sheet resistance value for implanted PET samples

Ion	Fluence (ions/cm ²)	Current (A) at 10V	Sheet resistance (Ω /sq)
Pristine		10^{-12}	10^{13}
Argon	2×10^{16}	1.65×10^{-8}	6.1×10^8
	8×10^{16}	7.5×10^{-8}	1.34×10^8
	1×10^{17}	1.86×10^{-7}	5.39×10^7
Titanium	2×10^{16}	8.56×10^{-8}	1.18×10^8
	8×10^{16}	1.09×10^{-5}	9.35×10^5
	1×10^{17}	1.17×10^{-4}	8.8×10^4

The values provided in Table 4-5 show an increase in the current and a decrease in sheet resistance with increasing ion fluence, where Drozdziel et al. reports a 5 orders of magnitude decrease in resistance for implanted PET by 135 keV Ar⁺ ions at 5×10^{15} /cm². The titanium implanted samples show a more dramatic increase in the current compared to argon. Implanted PET with Ti at 8×10^{16} has a much higher current than implanted PET with Ar at 1×10^{17} ; this could be because Ti is a metal and Ar a noble gas, and metals are known to have high conductivity values. The current increases with up to about 5 orders of magnitude for Ar and 8 orders for Ti at the maximum fluence from the pristine sample.

Figure 4-25 and Figure 4-26 show a relationship between resistances and the ion fluence. Both figures show a similar pattern where there is a dramatic difference in the resistance between samples implanted with 2×10^{16} and 8×10^{16} ions/cm². The difference between samples implanted with Ti at 8×10^{16} and 1×10^{17} is not as significant, these samples are observed to be at the same

level (more or less having the same resistance) and it is observed as having reached its saturation level or it has rather reached its percolation threshold.

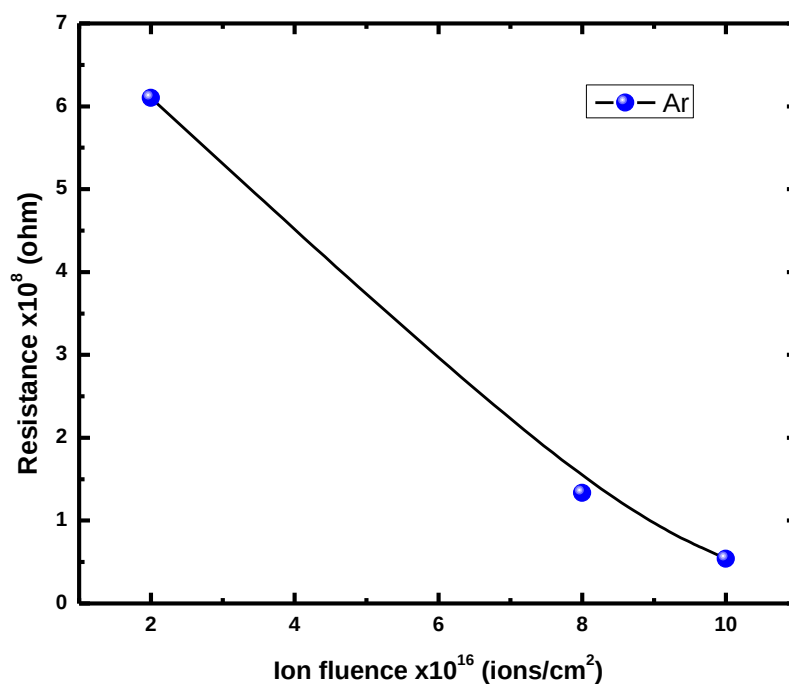


Figure 4-25: Plot of ion fluence versus resistance for Ar⁺ implantations

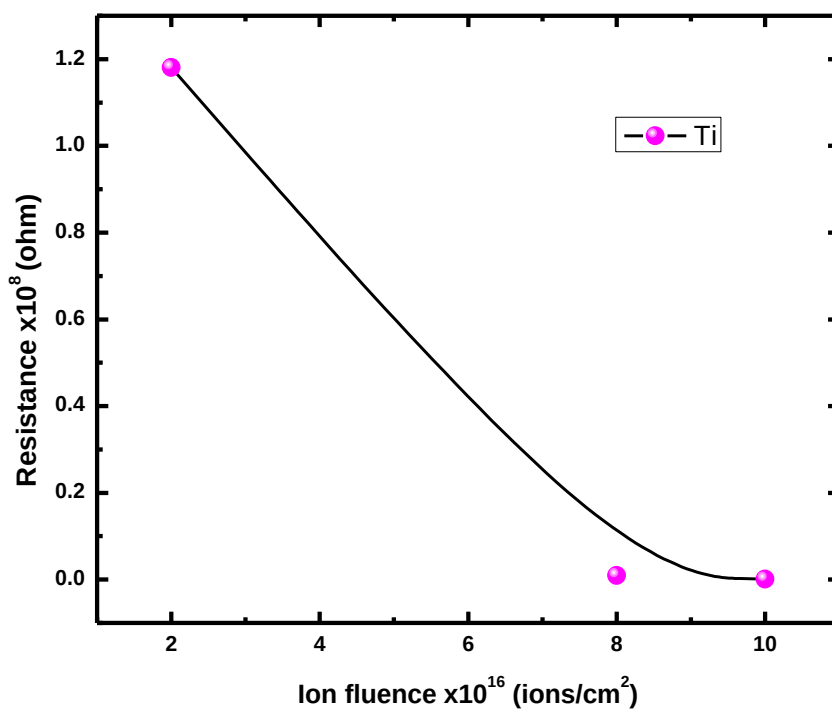


Figure 4-26: Plot of ion fluence versus resistance for Ti⁺ implantations

CHAPTER 5: CONCLUSION

The effects of ion implantation have resulted in changes in the chemical structure of PET. XRD data shows slight shifts in peak intensities, indicating small to no changes in the crystallinity of the film. It was also found that there is a small decrease in the crystallite size. There are similarities in the XRD data provided in this work with literature where PET samples are implanted at room temperature using different ions at fluences ranging from 10^{12} to 10^{18} /cm². From slight shifts in peak positions, to fluctuation in peak intensities and crystallite sizes with fluence. Results that were obtained through XRD do not provide a clear indication of ion beam effects in the polymer, thus being inconclusive. Bond weakening and breakage are explained by FTIR; destruction of some functional groups is confirmed by the disappearance of characteristic bands and wavenumber shifts, with Ti showing drastic changes with fluence. Breakage and disappearance of bands are reported in literature with samples implanted at RT; these reports show no significant differences from the work reported herein. Great damage in room temperature implanted PET is experienced by samples implanted at high energies.

The surface morphology of PET changes with fluence, from a smooth film to formation of granular materials and increase in roughness after ion irradiation and the gradual increase in the sizes of the grains. The content of C shows an overall increase given by EDX and HI-ERDA analysis. Small concentration in Ar is confirmed by both techniques, with Ti appearing quite well. Ar depth profiles show a surface diffusion of the ions while Ti ions have been implanted at a depth of ± 100 nm. SRIM predictions confirm the Ti experimental depth profiling.

Optical energy band gaps decrease with fluence for argon and titanium, thus there are increases in the Urbach energy and the number of carbon cluster. Similar decreases in optical band gap have

been reported in PET samples implanted at RT at different fluences, using different types of ions, and at different energies. PET experiences a redshift in this work; redshifts have also been reported in samples implanted at RT. The surface resistivity of the PET has been confirmed to be decreasing with fluence; this also constitutes an increase in the current flow thereby creating conductive pathways in the matrix of the polymer.

All experimental data confirm that the PET film has undergone some processes leading to the degradation of the polymer after implantation. These include scissions, cross-linking, bond breakage and other processes leading to carbonization of PET. Carbonization is proven by:

- the increase in granular materials observed in SEM
- the increase in C concentration in EDX and HI-ERDA
- breaking of bonds and destruction of functional groups in FTIR with an overall reduction in absorbance
- the decrease in E_g accompanied by increases in the E_u and N found in UV-Vis
- the decrease in electrical resistance and increase in current thus increasing the conductance of PET.

Temperature of ion implanted PET thin films show an insignificant effect on the properties of the polymer. The samples reported in this work, which are implanted at liquid nitrogen temperature have similar trends with samples that are reported in literature that are implanted at room temperature with the same fluence range. The energy reported in literature ranges from 3 keV to 120 MeV, using Ar, Ti, Ni, He, Ne, Ag, Si and C ions. Thus indicating that the cooling of the samples does not have an effect on the degree of damage that the polymer experiences. Substantial differences are observed in previous literature with changes in the implantation energy, where low

energy implanted samples experiences less damage than those implanted high energies. The implantation of PET results in the formation of nanoparticles resulting in an increase in the conductance due to carbonization as observed in section 4.7. The use of PET in semiconductor devices, including but not limited to nuclear and solar radiation sensor devices confirm these results.

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